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PAINTERS' OILS COLOURS AND VARNISHES

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PAINTERS' OILS, COLOURS, AND VARNISHES

WITH NUMEROUS ENGRAVINGS AND DIAGRAMS

EDITED BY

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1905

PREFACE.

PAINTERS' OILS, COLOURS, AND VARNISHES contains, in a form convenient for everyday use, a comprehensive digest of information, contributed by experienced chemists and colour manufacturers, scattered over the columns of BUILDING WORLD, one of the weekly journals it is my fortune to edit, and supplies concise information on the general principles and practice of the subjects on which it treats.

In preparing for publication in book form the mass of relevant matter contained in the volumes of BUILDING WORLD, much of it necessarily had to be re-arranged and re-written. However, it may be stated that a series of articles from the pen of Mr. H. B. Stocks, F.C.S., is incorporated in the text.

Readers who may desire additional information respecting special details of the matters dealt with in this book, or instruction on any building trade subjects, should address a question to BUILDING WORLD, so that it may be answered in the columns of that journal.

P. N. HASLUCK.

La Belle Sauvage, London,
February, 1905.

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PAINTERS' OILS, COLOURS, AND VARNISHES.

CHAPTER I.

PAINTERS' OILS AND VEHICLES.

In this work on the composition, properties and modes of preparing painters' oils, pigments, varnishes, driers, and similar products, it is proposed to describe the chemical reactions which occur during the production of the materials. It is always essential, before studying a technical subject, to obtain an insight into the rudiments of the sciences with which it is related; in the present instance a knowledge of chemistry, physics, geology, and mineralogy will be invaluable, as will be evident when it is remembered that painters' materials are of a very miscellaneous character, and are derived from the mineral, vegetable, and animal kingdoms.

The subject in hand may conveniently be considered under the following heads:—(1) Oils used in paint and varnish making; (2) pigments; (3) driers or siccative materials; (4), gums, resins, and varnish making.

The oils used by the painter are not numerous, but their extraction, purification, and subsequent treatment are very important and extensive industries, involving the use of special machinery and demanding a large amount of technical skill.

Oils are fluid and more or less viscous substances, varying considerably in colour according to the care taken in their extraction or subsequent purification. Some, such as castor oil, are colourless; some, such as olive oil, yellow or green; palm oil is orange; fish oils are brown; impure oils are black. The value of an oil depends largely upon its colour—the paler it is, the higher price it will command.

Oils have often a characteristic odour and taste; for instance, linseed oil, castor oil, and fish oils are by these simple tests readily detected. Oils are lighter than water, their density varying between ·913 and ·970 (water = 1).

Until recently the definition of the term "oil" was not an easy matter. In the early days of chemical knowledge the learned defined (and even at the present time the unlearned define) things more by their physical properties or outward appearance than by their composition; hence, as has been said, the term oil was applied to all unctuous or viscous liquids, including not only those bodies now known as oils, but also sulphuric acid (oil of vitriol), petroleum or rock oil, coal-tar oil, etc. At present the term oil is applied to two groups of substances—the volatile or essential oils, and the fixed or fatty oils. The volatile, or essential oils, such as those of lemon, bergamot, including also turpentine, distil unchanged on heating, hence their name; and as they mostly belong to one distinct group of chemical substances, one of the groups of hydrocarbons (that is, compounds containing carbon and hydrogen only) having the same or a similar composition to turpentine ($C_{10}H_{16}$), they are now generally called "terpenes."

Fixed oils are usually ranked along with the fats, which they closely resemble in all their properties; it is only at an ordinary temperature that any difference is perceptible, when the former are fluid and the latter solid; at a temperature of 150° F. they are all oily bodies.

Oils and fats are all "greasy" bodies; that is to say, when placed between two surfaces they adhere to both and yet cause the surfaces to readily slip away from each other, hence their value for lubricating purposes. They are incompatible with water; when oil and water come together they do not mix; water running over a fatty substance does not wet its surface. This property is extremely useful to the painter, because surfaces coated with oil paints and varnishes are thus protected from the destructive action of water.

The so-called oils of petroleum, coal tar, etc., belong to other groups of hydrocarbons, and are not true oils. The term oil is reserved for the fixed or fatty oils, which contain carbon, hydrogen, and oxygen, and decompose when heated to a high temperature.

Fixed oils and fats have a similar constitution, and when treated with re-agents behave in a similar manner. For instance, on treatment with sulphuric acid or with superheated steam, fatty acids and glycerine are produced; if heated with an alkali, the products are a soap or alkaline salt of fatty acids and glycerine.

Oils and fats are termed glycerides because they contain the radicle of glycerine (glyceryl C_3H_5), united with one or more fatty acids. A glyceride is represented by the formula of $C_3H_5F_3$, in which F represents a fatty acid; as there are three molecules of the fatty acid combined, the product is really a "triglyceride." Pure glycerides of different acids have names derived from the acids which they contain—for instance, the glyceride of oleic acid is called triolein $C_3H_5(C_{18}H_{33}O_2)_3$; similarly tristearin $C_3H_5(C_{18}H_{35}O_2)_3$ and tripalmitin $C_3H_5(C_{16}H_{31}O_2)_3$ are the glycerides of stearic and palmitic acids respectively. Oils and fats rarely consist of one glyceride; usually two or more are present in each, and the properties of the oils and fats depend upon the nature and the relative proportions of the glycerides present. Triolein is a fluid substance, and is present to a very large extent in many oils. On the other hand, tripalmitin and tristearin are solid, and their chief sources are the fats.

Certain oils have a well-marked peculiarity which has not hitherto been mentioned—namely, the property of "drying" or solidifying after exposure to air. Oils which show this property in a marked manner are found to consist largely of the glycerides of two acids known by the names of linolic acids ($C_{16}H_{32}O_2$) and linolenic acid ($C_{18}H_{30}O_2$); they therefore differ in composition from the "non-drying" oils, which consist principally of the glyceride of oleic acid.

It is a well-known fact that when certain oils are exposed to air for some time a gradual change takes place (familiarly known as "drying"), during which the oil changes from a fluid to a solid consistency, and, when spread in thin films, forms a varnish-like mass. Oils which undergo this change in a short space of time are known as "drying" oils; they are easily distinguished from non-drying oils, which remain fluid for an indefinite period.

The property of solidifying or drying is well marked in linseed oil, poppy oil, and a few others, but there are

many oils which show a slight tendency to dry or thicken on exposure, though they do not actually solidify ; for this reason they are classed as semi-drying oils. Only true drying oils are of any value as vehicles to the painter, their value depending largely upon the rate at which they dry, also upon the solidity and brilliance of their respective films.

Animal oils, and some vegetable oils, do not dry up by slow oxidation, but are converted into viscid or sticky masses having a rancid odour.

When the term "drying" is applied to the solidification of an oil, it is generally understood what takes place ; the term, however, hardly conveys a correct idea of the change. In ordinary drying processes, some liquid —such as water—evaporates, leaving the solid matter dry ; but in the drying of an oil no part evaporates—on the contrary, there is always a gain of weight. In the act of drying, the oil must therefore absorb something from the atmosphere ; it was discovered by De Saussure that the gain was due to the absorption of oxygen. The varnish-like film is an oxidised product of linseed oil. It was called by Mülder "linoxyn," but up to the present its composition is not with certainty known. That oxygen is really essential during the drying process is soon apparent if a film of oil is exposed in a jar of air ; the oxygen is rapidly absorbed, and the film remains sticky for an indefinite period unless a quantity of fresh air is admitted.

The process of oxidation or drying is retarded by a low temperature, and it is well known to painters that warmth and a good circulation of air are necessary during the drying of paints and varnishes in which drying oils are essential ingredients.

Attempts to hasten the drying of paint oil soon made apparent the following facts:—It was found that the drying was quickened by heating the oil for some hours ("boiling"), and, further, that certain metallic salts had the power of aiding the absorption of oxygen very materially. These bodies are principally the salts of lead and manganese, the oxides of these metals being specially valuable. Their action is somewhat obscure, and various theories have been put forward to explain it. They seem to act as carriers of oxygen rather than simple oxidising

agents, a very small proportion having a marked effect on the oil; but the exact reaction is yet to be determined.

Among vegetable oils, the best known and most commonly used are—linseed, cottonseed, hempseed, rape or colza, castor, poppy oil, and nut oils. Their suitability for mixing with pigments for paint-making depends on their drying properties, and under this head seed oils in general may be classed, though that property in, say, rape oil is, practically speaking, *nil*, and in others, like cottonseed, is very weak. One or two nut oils also come into this group, but of the lot the only one used commercially in paint-making, it may be fairly said, is linseed oil. Poppy oil is a good second as regards drying, and is used in preference to linseed oil by artists on account of its pale colour; but its cost prevents more extended use.

Linseed oil is the product, obtained by expression from seeds, of the flax plant (*Linum usitatissimum*). The plant is grown to some extent in England and Ireland, and largely in Russia, the East Indies, and America. The flax fibre is used in linen manufacture. Flax seed, or linseed, is a small ovate seed, having a hard, brown, shining exterior, and a soft mealy interior. The seeds usually contain an admixture of seeds of other plants, which are extremely difficult to remove. These latter are derived from plants growing alongside the flax plants, or they are intentionally added as adulterants. Some of the foreign seeds may be removed by passing the whole through sieves, as may also small particles of sand and other impurities.

Several varieties of linseed oil are known in commerce, such as "cold pressed," "raw," "artist's oil," and "boiled oil." Linseed oil varies very much in colour. When pressed in the cold state or after bleaching it has a very pale yellow colour; ordinary raw oil is dark yellow; boiled or impure oil is reddish brown. The odour and taste of the oil are very characteristic. The specific gravity of linseed oil varies between ·932 and ·937, and, as before stated, the principal constituents are the glycerides of two fatty acids—linolic and linolenic acids.

Poppy oil is prepared from seeds of the poppy (*Papaver somniferum*) by expression in a similar manner to linseed oil. Poppy oil is inodorous, possesses a straw-yellow

colour, and its flavour resembles that of almonds. The specific gravity of this oil ranges from ·924 to ·927.

Walnut oil is obtained from walnuts, the seed of the *Juglans regia*. The shells are removed and the kernels subjected to pressure, the yield of oil being about 50 per cent. of the weight of the nuts. Walnut oil, extracted from fresh nuts by cold pressure, is nearly colourless, or a pale green, and possesses a very mild taste and odour; but when hot pressed or derived from rancid nuts it is dark in colour. The specific gravity of walnut oil is about ·925. In composition and properties, poppy oil and walnut oil closely resemble linseed oil; they are both excellent drying oils, and, having a pale colour, they are used by artists for making flake white or delicately tinted pigments.

The oils that show only a slight tendency to dry are not used as media by the painter, owing to the fact that they remain sticky for an indefinite period; they are, however, often used as adulterants. When added to drying oils in an appreciable quantity they are extremely detrimental to the hardness and brilliancy of the film produced on drying. Cotton-seed oil, niger seed oil, and others are in this way employed; sometimes resin oil, mineral oils, fish oils, and common resin are used for a like purpose. The detection of these adulterants is a difficult branch of analytical work; but a useful and simple test of the value of a drying oil is to determine its drying properties.

Oil to be tested for drying qualities should be poured upon a sheet of glass and spread evenly with the finger. On being heated in a steam oven to a temperature of 212° F. the oil should dry hard in a few hours; any tackiness remaining would condemn it for painting purposes.

Acids have a powerful action upon linseed oil when added to it in a concentrated state; strong sulphuric acid causes it to thicken and become black. A considerable rise takes place in the temperature, and sulphur dioxide is evolved. The rise in temperature is more than 180° F., and serves to distinguish it from most other oils, which do not react so violently. This test is known as Maumene's test (see p. 34).

Strong nitric acid rapidly oxidises linseed oil, nitrous fumes being evolved; if the action is allowed to go on unchecked the mass may possibly take fire.

Nitrous acid gives a dark fluid product with linseed oil and other drying oils, whereas with non-drying oils the mass is pale yellow and solid; this test, which serves to

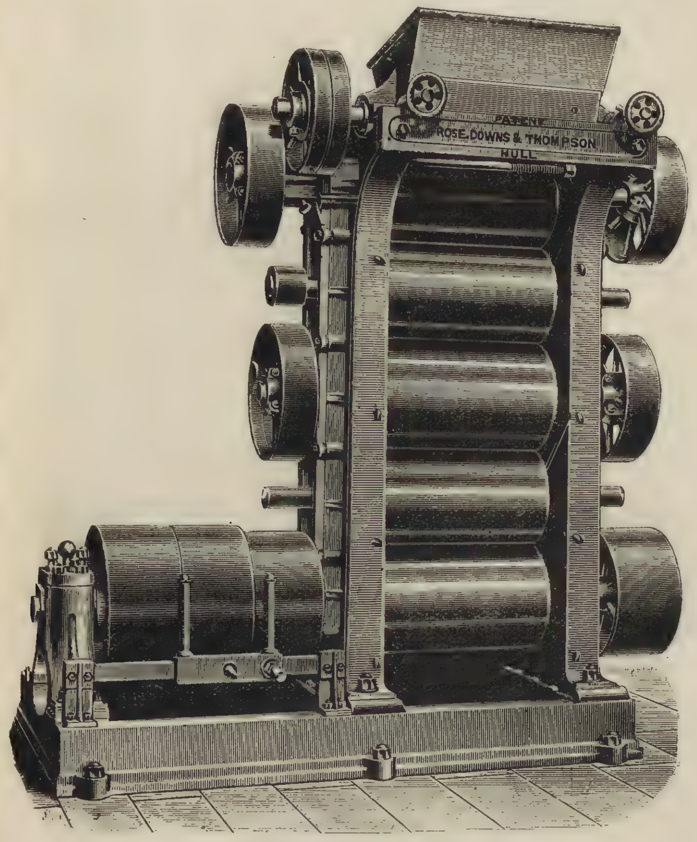


Fig. 1.—Seed-crushing Rolls.

distinguish the two classes, is known as the elaïdin reaction.

The elements, chlorine, bromine, and iodine also act energetically upon drying oils; Hubl's test consists in

determining the amount of iodine absorbed by oils. Linseed oil absorbs the greatest amount; 100 parts of oil absorb about 158 pts. Semi-drying oils absorb less iodine; cotton-seed oil takes up from 105 to 109 parts of iodine. Non-drying oils require very much less olive oil, only 82

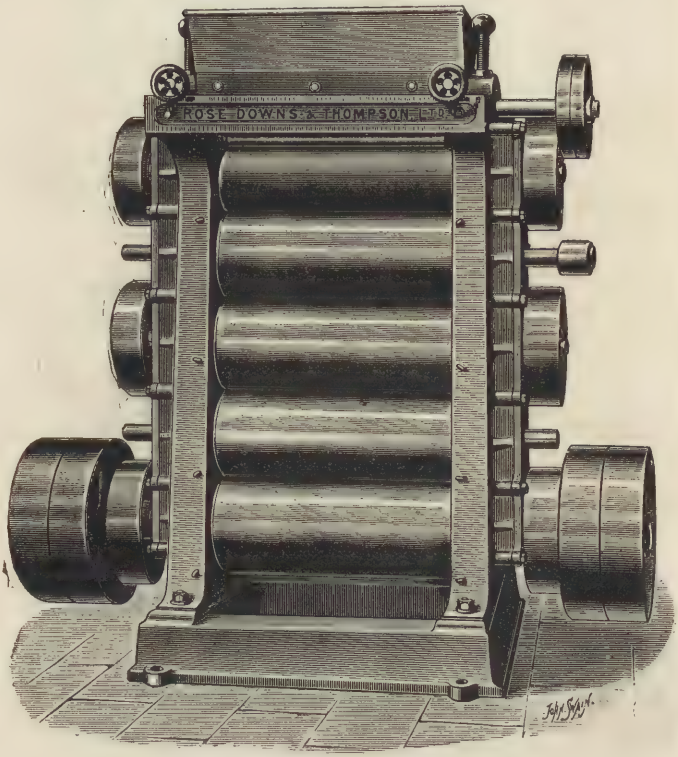


Fig. 2.—Seed-crushing Rolls.

parts being absorbable. This test is probably the most useful one with which to ascertain the purity of oils.

The methods employed for extracting linseed oil are typical for the whole series of vegetable oils, and it therefore will be useful to consider them in detail.

Linseed oil is extracted by two methods, one English, the other Anglo-American, but they vary only in detail.

In the Anglo-American system, which is becoming general, the seed is crushed by being passed through a

Fig. 3.

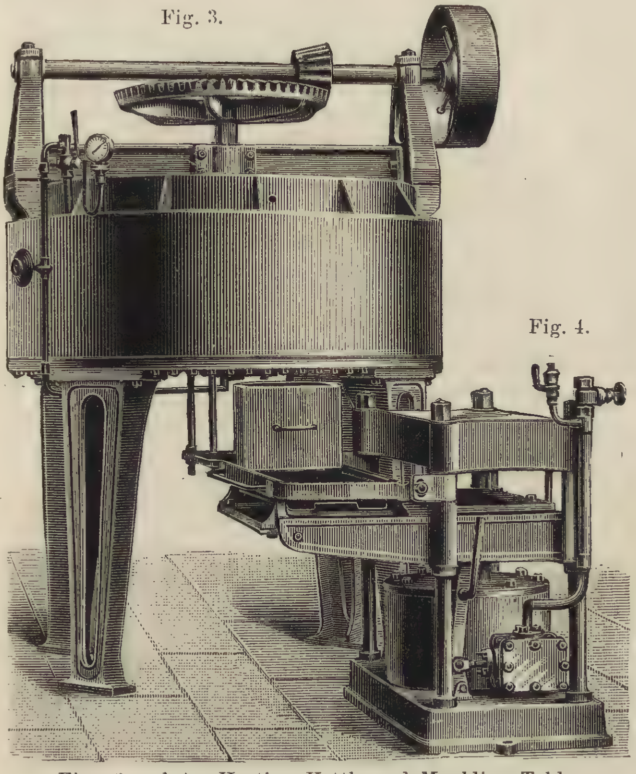


Fig. 4.

Figs. 3 and 4.—Heating Kettle and Moulding Table.

series of iron rolls, as illustrated by Figs 1 and 2. It is first poured into the hopper at the top, from which it is fed to the first and second rollers. In these the seed is crushed; the meal, passing through the other rolls, is submitted to a gradually increasing pressure as it descends. The

crushed meal is next placed in the kettle (Fig. 3), which consists of a circular metal pan, steam jacketed and supplied with agitators which are worked by toothed wheels above. The crushed seed is heated in the kettle to a temperature of 170° F. by means of steam, and the agitators are kept in motion to bring the whole of the meal to a uniform temperature. By opening a slide in the bottom of the kettle a certain portion of the heated meal is allowed to fall into a measuring box, thence on to the moulding table (Fig. 4). Here it is gently pressed into shape by hydraulic power, and the excess of meal is returned to the kettle. The cake of meal is placed between two corrugated iron metal plates having the name and trademark sunk therein, and the plates and contents are then conveyed to the hydraulic press (Fig. 5). The meal is, in some cases, submitted to a moderate pressure at first; afterwards the pressure is increased. The oil, as it escapes from the meal, falls down into the tank in which the press is placed, and from thence it is pumped into large storage tanks. Of the two Anglo-American oil presses shown by Figs. 5 and 6, the second is the more modern.

The system as above described is the result of a slow process of evolution. The older forms of press were of wood, and the pressure was applied either by a lever or a weight, and later by what was known as a "plunger," which was a falling weight capable of driving two wedges together and thus gradually applying pressure to bags in which the meal was placed. Elbow-presses and screw-presses have also been employed, but these are now superseded.

In the English method of extraction the meal is enclosed in canvas bags which are covered with horse-hair cloths and then pressed; the bags, however, are very liable to burst under great pressure, and for this reason the system is going out of use.

The linseed-meal cakes obtained by the pressure treatment still contain from 7 to 10 per cent. of oil, or, in exceptional cases, perhaps as low as 5 per cent., and they are largely used for feeding cattle.

Another method of extracting linseed oil may be mentioned. The crushed seed is fed into a series of cylindrical tanks in which it is treated with benzine, petroleum spirit,

or other solvents for fat, the apparatus being heated by steam. The solvent enters the first tank, in which the meal is almost exhausted of fat, and passes right through the series until finally it reaches the untreated meal; in

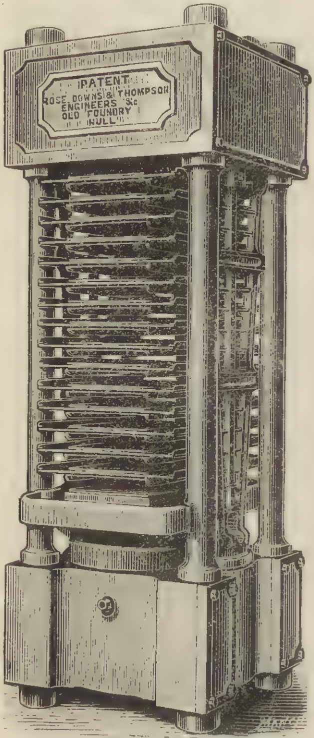


Fig. 5.

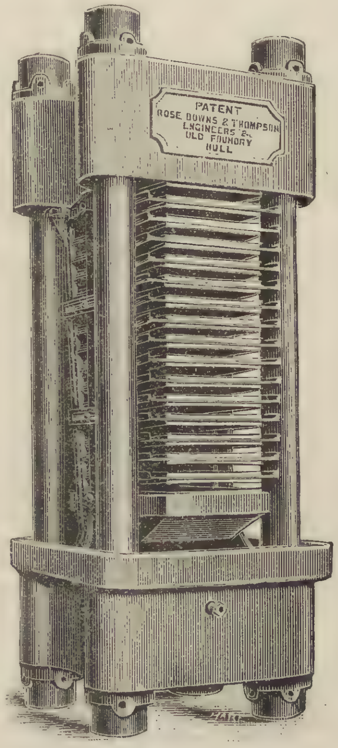


Fig. 6.

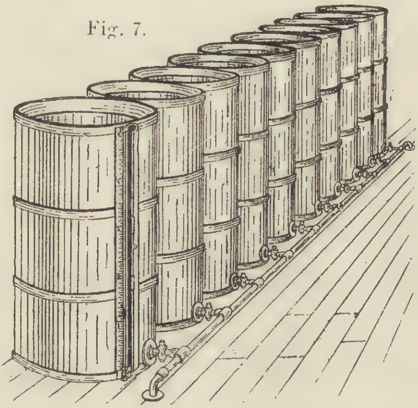
Figs. 5 and 6.—Anglo-American Oil Presses.

this way the solvent becomes saturated with fat, and, by evaporating the former in a distillation apparatus, the oil is left behind. By this method practically the whole of the oil is removed from the meal, and therefore it is very economical; but this is not wholly an advantage, because

the meal, being entirely deprived of oil, is of no value as a feeding stuff; the oil retains the odour of the solvent and appears to be of inferior quality, and so the process has not found much favour.

Freshly expressed linseed oil is by no means fitted for use in the arts either in the "raw" condition or for boiled oil or varnish making; it is usually stored for a considerable period before being used. The storage tanks are arranged in series with pipes running alongside for drawing off the oil. The installation shown in Fig. 7 is of 5,000 gals. capacity, designed by Messrs. Oxley, of Man-

Fig. 7.



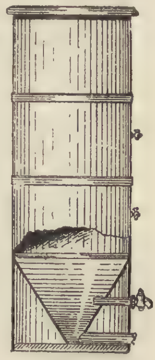


Fig. 8.

Figs. 7 and 8.—Storage and Settlement Tanks.

chester, who have made a special study of the plant used for this branch of the manufacture. The settling tank (Fig. 8), also made by Messrs. Oxley, is designed for the better separation of the suspended matter, which, on standing, deposits in the cone-shaped vessel, and is then prevented from passing out with the clarified oil.

The freshly expressed oil contains certain impurities, the presence of which unfit it for use in that state; it is therefore necessary to put the oil through certain operations with a view to its purification.

The impurities existing in the raw oil consist of finely divided portions of cellular tissue, fibre, husk, etc., an

albuminous or mucilaginous substance, and colouring matters. By storing the oil as before described, the greater part of the suspended matter is separated; subsequently the oil is filtered by passing it once or twice through a filter press. The filter presses used in oil works are shown by Figs. 9 and 10, the former being sufficiently small to work by hand; the latter is a more powerful press worked by steam power. The plant illustrated in this chapter for extraction of oil and the filter presses are made by Messrs. Rose, Downs and Thompson, of Hull, to whose kindness is due the use of some of the illustrations.

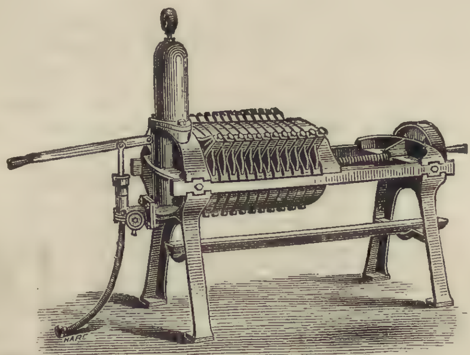


Fig. 9.—Hand-power Filter Press.

The filter press consists of a framework supporting a number of iron plates. These plates are recessed, so that when they are all screwed up tight by the wheel—seen to the left of Fig. 10—they form a series of shallow chambers. The plates are also grooved with channels to allow the oil to escape, and when in use are covered with two layers of a special filtering cloth held in position by fasteners. The cloth used in the oil presses is of two kinds: the inner a very strong material and closely woven, while the outer material is more open in texture. After the filter cloths are fixed in position, the plates are screwed up tight by revolving the wheel. The oil is now pumped into the press, and, after passing through the filter cloths, it runs down the grooves and drips into the trough below.

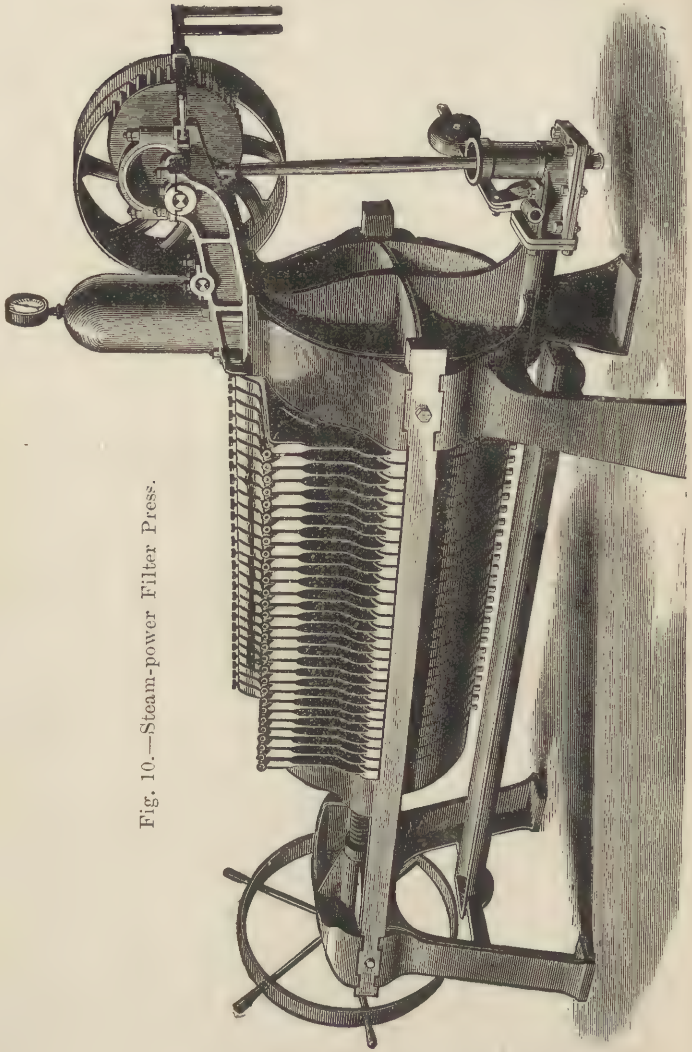


Fig. 10.—Steam-power Filter Press.

The filter press is not opened until the finely divided material which is filtered out impedes too much the flow of the oil. After a time this material collects to such an extent as to choke the filter, which has then to be opened. The filter cloths have to be removed and scraped clean before they can be again employed. After storage and filtration, the oil becomes quite clear and bright, but it is still coloured to some extent. For most purposes, however, this oil is sufficiently purified to be used, and it is known in commerce under the name of "raw" linseed oil.

There are several other methods of purifying linseed

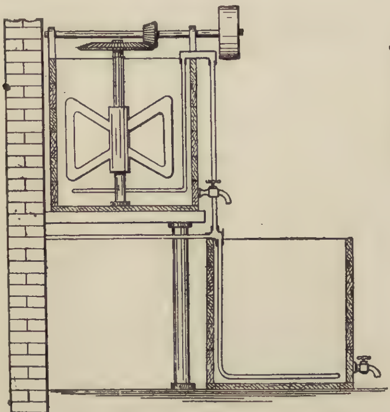


Fig. 11.—Oil-purification Plant.

Fig. 12.—Oil-boiling Pan.

oil, in which certain chemicals dissolved in water are agitated along with the oil, and then the latter is allowed to clarify by settlement, the object being to coagulate and precipitate the albuminous matter which appears to be dissolved in the oil, and at the same time carry down the suspended matters. The substances used for this purpose are alum, zinc sulphate, etc., and, more important still, sulphuric acid.

The plant used for purifying linseed oils with sulphuric acid is shown by Fig. 11, and consists of two large tanks built of wood lined with lead. The upper tank is placed upon a platform and is provided with stirring gear, and

also a coil of lead pipe perforated with small holes; the lower tank is provided with a similar coil, both coils being connected by iron piping to a boiler. The oil to be purified is first run into the upper tank, and sulphuric acid is then added. Concentrated acid has been tried, but it is too local in its action, charring and blackening that portion of the oil with which it first comes in contact; it is therefore usual previously to dilute the acid with four or five times its volume of water, which modifies its action and prevents the charring of the oil. The amount of acid used is from 1 to 2 per cent. of the weight of the oil. After the addition of the acid the agitating blades are set in motion and the whole thoroughly mixed. Steam is now blown in through the coil of pipe, and after some time the oil is left to repose, run into the lower tank, and again steamed; after a second period of repose, the oil is either heated in a steam-jacketed pan to remove the last traces of water, or it is stored for a time for a similar purpose. The oil thus purified is quite clear and bright, and of a pale colour.

For special purposes—as, for instance, for the use of the artist—an almost colourless oil is required, and this is obtained by exposing the oil to the bleaching action of air and light; the oil is exposed to direct sunlight under glass roofs in large shallow metal trays, the depth of oil being about 9 in. In this method of treatment the operation is accelerated by placing strips of lead in the tanks or by the addition of small quantities of lead acetate. The method of bleaching linseed oil just mentioned, though producing a very pale oil, is nevertheless not generally applicable, owing to the large amount of space required and the time occupied; the sunlight required is also not always obtainable, and in the winter time the bleaching operations are at a standstill. It is important to expose the oil for a certain period as experience dictates, otherwise it gradually becomes coloured again.

Besides the methods mentioned, there are several other ways of purifying or otherwise improving linseed oil, but, with the exception of the Hartley-Blenkinsop method, which is fully described later in this chapter (see p. 29), it will not be necessary to refer to them in detail.

The term "boiled" oil is given to the product which is formed when raw linseed oil has been heated or "boiled"

for some time; certain agents are added during the boiling with the object of accelerating the drying of the boiled oil. The agents added are usually compounds of lead and manganese, to which the term "driers" has been applied; boiled linseed oil is also known as a "drier."

The raw linseed oil to be used in the manufacture of boiled oil or in the production of varnishes is best if prepared from fully ripe seed. It must previously have been stored for a considerable period, and subsequently thoroughly refined; newly expressed or imperfectly refined oil usually spoils the product. It is especially necessary in the previous refining to remove entirely the albuminous matter, otherwise it is extremely liable to separate or "break," forming lumpy masses, which settle upon the bottom of the pan, and, there becoming charred, impart to the oil an unduly dark colour.

The operation of boiling oil, though simple in principle, is not an easy one, and it often happens, even when all precautions are taken, that the boiled oil is not as it should be; there are variations in the product which are not always easy to account for. The industry is, therefore, one in which highly experienced workmen are required. There are two methods of boiling linseed oil—the old method of fire boiling, in which the oil is heated by an open fire, and the newer method of steam boiling in jacketed pans. Both methods are now in extensive operation.

The pans used in the open fire system of boiling the oil resemble an ordinary washing copper, being built in brickwork and provided with a fireplace and chimney. To minimise the risk of fire—a danger which is always present in oil boiling—it is better to have the fireplaces on the outside of the boiling shed, as there is then practically no danger if the oil should boil over. The pans are covered with hoods connected to a chimney, for the purpose of carrying off the disagreeable and unhealthy fumes which arise from the hot oil. The boiling pans are made either of cast-iron or of wrought-iron boiler plates riveted together, with the bottom made all in one piece, and their capacity varies with the size of the works, from 100 gal. up to 600 gal. Fig. 12 (p. 23) represents in section a common form of oil-boiling pan.

The boiling pan is about two-thirds filled with the raw

linseed oil. Not more than this quantity is heated at one time, because the oil not only expands in heating, but froths a good deal, and is liable to boil over. The oil being placed in the pan, the fire is kindled and the heat gradually raised. Throughout the operation the oil is continually stirred with a paddle to equalise the temperature of the mass. This continual stirring is one of the essentials of success, as the heated oil circulates but slowly, and, unless constantly stirred, may become highly heated and charred at the bottom. Water and other vapours are freely evolved during the heating, but any undue frothing is kept down either by beating it with a kind of whisk, or by removing some of the oil with a ladle and pouring it back from a height. The heating up takes about two hours, and, after the frothing ceases, the oil is allowed to boil quietly for three hours, when the addition of the driers is begun.

The driers are added in small portions at a time, with vigorous stirring to prevent them caking on the bottom of the pan. The fire is still kept up till the man in charge—the oil boiler—can tell that it is finished. This he does by dipping a feather into the oil, which, if sufficiently boiled, will shrivel it up.

Next day, the film on the surface of the oil is skimmed off, and the oil, still quite hot, is run into tanks, where it is usually stored for a few weeks to become quite clear and bright by settlement. The driers added are litharge, acetate of lead, sulphate of zinc or umber, etc., one or more, according to requirement. The amount of driers added varies somewhat, but about 5 lb. per ton of oil is a usual quantity. The temperature of the oil should be kept as uniform as possible during the boiling, and as low as possible, consistent with good results, in order to avoid charring or darkening the oil too much. The temperature is generally about 500° F., but in special cases this may be raised. The temperature is now usually recorded by a special varnish thermometer, of which there are many forms. One of these, manufactured by James Murray and Co., of Glasgow, is shown in Fig. 13.

The fumes evolved from the boiling oil consist of water vapour, acrolein, formic and acetic acids, etc. They are chiefly derived from the radicle of glycerine contained in

the oil, and, as before stated, they are carried off by the hoods placed over the pans.

In order to obviate the great risk always attendant upon oil boiling by open fires, and also the drawback occasioned by the deep discoloration of the oil, several inventors have devised methods whereby the oil may be boiled by steam. The pans used for boiling oil by steam are in some cases hemispherical, with a steam jacket reaching to the level of the surface of the oil, and a large cock underneath the pan for removing the finished product. These pans are, of course, covered with a hood for carrying off the vapours evolved. Fig. 14 shows a pan of this kind manufactured by Messrs. Brinjes and Goodwin, who have kindly lent the block, as well as some others shown in this book.

Fig. 13.

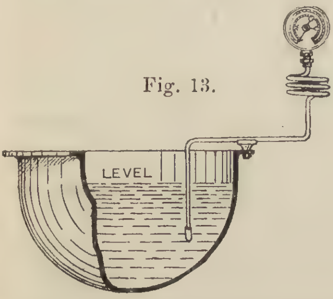


Fig. 13.—Varnish Thermometer.

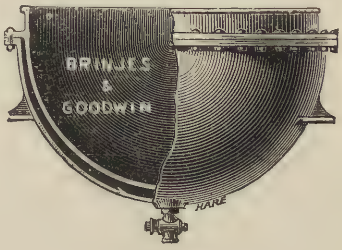


Fig. 14.

Fig. 14.—Steam-jacketed Boiling Pan.

Many years ago Mr. Vincent manufactured oil by this method for the *Illustrated London News*, and the plant used was similar to that shown by Fig. 15. The pan A is made of copper, provided with a steam jacket B reaching to about half of its height. The pan is covered with a hood C, in which there are three openings. The centre opening contains a stuffing-box, through which passes a shaft E reaching to the bottom of the pan. The shaft consists of a solid rod inside a hollow one, each rod being provided with arms F, which are caused to revolve in opposite directions by suitable gearing at the top of the shaft. Through the opening G, closed with a lid during operation, the oil and driers are added, and the third opening H carries a pipe for conveying the fumes to the

fireplace, where they are burnt. The pipe I conveys the steam to the jacket, and the perforated coil J serves to introduce a blast of air blown by an engine. The cock K is for emptying the pan.

In connection with the boiling pan, a tank is provided capable of holding one batch of the oil—that is, from 2 tons to 3 tons; and, while a previous charge is boiling the waste steam from the jacket passes through a coil of pipe in this tank, and serves to raise the temperature of the oil to about 95°. The boiling pan being emptied, the charge of oil from the tank is pumped in, and steam at a pressure of 35 lb. turned on; the agitators are set in motion, and when the proper degree of temperature has been reached, air is blown into the oil, and the man-hole in the hood is closed. The oil froths up considerably during the boiling, and gradually becomes more viscid; the driers, previously mixed with some oil, are added during the operation; after which the boiling proceeds for about four hours, and the oil is then run off by the cock through a detachable pipe into a tank, from which it is pumped into the store tanks, where, after a few weeks' settlement, it becomes clear and bright. The amount of driers added ranges from 5 lb. to 15 lb. per ton of oil.

Binks invented, many years ago, a method of producing boiled oil at a very low temperature. The plant used in this instance consists of a vat made of wood lined with lead and provided with a false bottom, into which steam may be blown for warming the oils; there is also, passing down into the tank, a pipe through which a current of air is blown into the oil. Several tons are heated in the tank to a temperature of 100° to 150° F., and hydrated manganous oxide, or materials which will produce this compound, are added as driers, air being passed in. Mr. Binks stated that an oleate of the manganous oxide was formed, which removed oxygen from the oil and carried down the colouring matter, leaving a very pale product. This theory is opposed to the one generally held, that it is necessary to add oxygen to the oil in order to increase its drying properties. It is most probable that the manganous hydrate acts as a carrier of oxygen to the oil in the same way as other driers. This point will be more fully discussed when the driers are described.

Later, Messrs. Hartley and Blenkinsop patented a process for bleaching and at the same time boiling linseed oil. In this process the oil is first treated in a tank with sulphuric acid of 30 per cent. strength, which is found to char the impurities without injuriously affecting the oil. After being washed and allowed to stand for some time the impurities subside, the oil is heated in a special tank, and manganous linoleate, dissolved in turpentine or other solvent, is added; and, at the same time, a current of air or oxygen is blown through the oil. The air, in conjunction

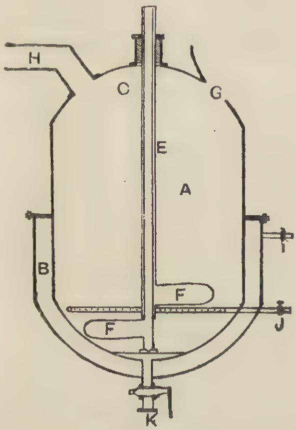


Fig. 15.—Vincent Oil-boiling Pan.


Fig. 16.—Separating Funnel.

with the manganese compound, first bleaches and then converts it into an excellent drying oil. By varying the time of heating, products of any desired consistency may be obtained. The amount of manganese linoleate added is very small; as already stated it is not added neat, but in the form of a solution.

Among the many processes for boiling linseed oil not yet mentioned, that patented by Wilson, in 1879, was for bleaching and oxidising oils by means of a current of ozonised air or oxygen, assisted by steam heat; by means of Hadfield's process (1887) the oil is heated and then passed down a pipe in the form of stream or spray, en-

countering in its passage a current of air travelling in the opposite direction.

The chemical effect of boiling linseed oil is somewhat obscure. The products given off are, first, water; then, as the temperature rises, this is accompanied by fumes of formic acid, acetic acid, and the pungent smelling acrolein, these substances being produced by a partial decomposition of the glyceryl radicle contained in the oil; at the same time a small quantity of the free acids are liberated, which combine with the metallic substances added as driers to form linoleates of either manganese or lead as the case may be. These metallic linoleates remain dissolved, in the oil, and as they have a powerful affinity for oxygen they cause it to dry rapidly.

According to Vincent, oil boiled without driers does not dry rapidly, but it has been found by independent experiment that an oil boiled for three hours, with air blown through, forms a moderately good drying oil. Excellent drying oils were also prepared by adding manganese and lead linoleates to raw linseed oil which was kept at a temperature of 80° to 90° F. for a few hours. The decomposition of the oil on heating, and the liberation of the linolic acid, are only partial; and whether it is to be assumed that the increased drying properties result from this cause alone, or whether they are to some extent due to the stability of the compound being broken by partial decomposition, or, again, whether they are due to polymerisation, as suggested by some chemists, is not at present settled. These details need not be further discussed, as they require experimental proof, but further particulars will be given in the chapter on driers.

Boiled oil has peculiar properties, particularly its power of drying to a hard film in less than twenty-four hours, whereas the raw oil remains "tacky" for a longer time than this. The film obtained on drying is brittle, but raw oil forms an elastic coat; the latter is preferred for this reason where it is possible to use it, and it is added in mixing paints either alone or in conjunction with boiled oil.

Boiled oil is very viscous, and has a higher specific gravity than the raw oil, namely, about ·940. It is of a dark reddish-brown colour when prepared over open fires, but steam-boiled oil is little, if any, darker than the raw

product. It has a characteristic odour and an acrid taste. Boiled oil is liable to be adulterated with the same materials as the raw oil.

Many attempts have been made to produce substitutes for boiled oil; but without entering into details of their manufacture, it may be stated that many of these substitutes contain boiled oil as an essential ingredient. Other materials used in conjunction with this are resin, resin oil, and resin soaps; and sometimes turpentine or resin spirit is present. One illustration of the composition of these products is given in the patent of Wilson, whose proposed substitute consists of a solution of resin in a mixture of soda crystals (carbonate of soda), ammonia, and water.

Wood oil, also known as Chinese wood oil, tree oil, oil varnish, and tung oil, has been introduced during the last few years as a substitute for linseed oil, principally in the manufacture of varnishes, paints, lacquers, and oilcloth. Wood oil is obtained from the trunk of the East Indian *Dipterocarpus turbinatus*, and is known also as gurjun balsam. Owing to the high price of linseed oil, many of the leading experts have investigated the properties of wood oil, the result of these observations varying considerably. Wood oil requires extreme care when used in the manufacture of oil varnishes, as it gelatinises at a temperature of 180° C., and is then useless for manufacturing purposes. Another fault in wood oil is that when used alone or with linseed oil it assumes a whitish cast, this being particularly noticeable when exposed to atmospheric influences; also in a damp atmosphere it loses its adhesion somewhat, but hardens again when exposed to warm air or sunlight.

To make Chinese wood oil a commercial article for varnish making requires a special treatment to prevent it peeling. The method is as follows. The oil is first heated for two hours at 170° C., and then placed aside to repose for fifty hours, when the clear top portion is ladled off; this is known as clarified oil. The clarified oil is then heated to 180° C. for about one hour or until it slightly thickens, and is then allowed to cool down to 140° C.; 2 per cent. of finely-ground litharge is then added and the whole thoroughly agitated. It is then allowed to cool to about 95° C., and is thinned down with American turpentine. The resulting varnish dries in about six or eight

hours. Resin, manila, or dammar gums may be added to the varnish, in quantities varying from 50 per cent. to 75 per cent. ; these render the varnish hard and elastic, and it dries in eight or ten hours with a hard transparent gloss. Wood-oil varnishes are more resistive to atmospheric influences when worked up with pigments ; these varnishes are also useful in the preparation of enamels, especially when incorporated with zinc white. In the preparation of lacquers wood oil is also very useful, as it possesses the remarkable property of being soluble in amyl alcohol, which renders the oil valuable in the lacquer industry. Many attempts have been made to deodorise wood oil, but up to the present without success ; the odoriferous principles are the result of oxidation.

A reliable test for both raw and boiled linseed oils is the flash test, the temperature at which linseed oils usually flash being 470° F., whilst mineral oil, which is the chief adulterant of linseed oil, flashes at about 400° F., and resin oil still lower, thus rendering it a simple method to detect these adulterants.

The alkalies, when heated with linseed oil, decompose it and forms soaps of fatty acids (linolic and linolenic acids) and glycerine. This reaction is common to all oils and fats ; the amount of alkali required varies slightly, but it serves to detect the presence of mineral or resin oils, which are not saponified, and therefore are easily extracted from the soap by means of ether.

If it is desired to ascertain the amount of these adulterants in linseed oil, take any weight of the suspected oil, place it in a beaker or any suitable vessel, and add a small quantity of caustic soda, alcohol, and a little water. The contents of the vessel should then be boiled for some time, with constant stirring, after which the oil will be found saponified whilst the adulterants will be unchanged. The mass is then poured into a separating vessel (Fig. 16) and agitated with benzine until it takes up the mineral or resin oil, which afterwards comes to the surface of the vessel. The bottom layer is then run off and the top portion is well washed with warm water until all traces of the saponified oil have disappeared. The residue, which is mineral oil, is then placed in a vessel and weighed.

Much common resin is also used as an adulterant, and

may easily be detected, if in any considerable quantities, by painting a small quantity of the oil on any glass surface and, when it is thoroughly dry, rubbing well with the finger; if the oil contains much resin it will rub up and crumble, whilst a good oil will not be affected.

Another method which is very reliable is to find the specific gravity of the sample of oil. The average specific gravity of linseed oil varies between 0·932 and 0·937, and if it is less than 0·932 the oil is evidently adulterated with cod, mineral, or niger seed oil, and the specific gravity exceeding 0·937 indicates the presence of resin oil. Most other oils that could be used as adulterants of linseed oil have a lower gravity, cottonseed and hempseed oils being ·930, walnut oil ·929, poppy seed oil ·924 to ·927, sunflower seed oil ·925, earth nut ·918, and colza ·914. To get any result from the weight of a gallon of the oil it would be necessary to measure the oil very carefully; a gallon of linseed oil will weigh from 9 lb $5\frac{1}{8}$ oz. to 9 lb. 6 oz. nearly, as against 9 lb. 4 oz. for cottonseed oil, so that there is very little margin for error.

Another test for the purity of linseed oil (apart from chemical tests) is to examine its drying properties; this may be done by spreading a very thin layer of oil upon a glass plate, and exposing it in a warm situation. Boiled linseed oil will be dry in twelve hours or thereabouts, but raw linseed oil will require two or three days. Prepared boards may be also used for the purpose, in which case the time will be somewhat shortened. It is a good plan to compare the samples with undoubtedly genuine boiled or raw oil.

The drying power of oils is directly proportional to the amount of oxygen they are capable of absorbing, hence Livache's test is a good one for the purpose. A large watch glass is taken, and upon it is spread about 1 gramme of precipitated lead; the watch glass is then weighed, the oil, about ·6 gramme or ·7 gramme, is dropped upon the lead, and the whole weighed to get the exact amount of oil taken; the watch glass is then exposed to light in a place free from dust; after two days the glass may be again weighed. Linseed oil treated in this manner gained 14 per cent. in weight, while walnut oil gained only half that amount, and the other oils much less.

Maumene's test, noted on p. 14, is also very useful and is easily performed; 50 grammes of the oil are weighed out into a beaker, and this is placed in a larger beaker, the space between the two being filled with cotton wool; 10 c.c. of concentrated sulphuric acid are run gently into the oil from a burette, the oil being stirred with a thermometer during the operation. The oil is charred and decomposed by the acid, the temperature rising considerably; linseed oil yields a rise of temperature of 103° to 124° C. Some of the fish oils give an equal or even a greater rise, but the other seed oils are much lower, cottonseed oil being about 75° C. To determine the rise, the temperature of the oil before the experiment is deducted from the highest temperature recorded.

The presence of resin oil in linseed oil is best determined by the Liebermann-Storch reaction. 1 or 2 c.c. of the sample of oil are mixed with acetic anhydride, a gentle heat is applied and the tube shaken; after cooling, the acetic anhydride is removed and a drop of strong sulphuric acid added to it. Should resin oil be present, a violet colour will develop. Linseed oil alone yields a green colour, and the test is a characteristic one. Stannic chloride yields violet. The amount of resin oil is determined as follows:—5 grammes of the oil are weighed into a large porcelain dish, and 25 c.c. of alcoholic caustic potash solution (84 gammes per litre) are added, and the whole heated on the water bath with constant stirring until the vegetable oil is saponified; the liquid is cooled and water added, the soap solution is poured into a separating funnel (Fig. 16) and the dish washed out with water which is also run into the funnel. The liquid in the separator is now cooled and petroleum ether added; the two liquids are shaken together, and when the ether rises to the surface it contains in solution all the resin oil. The lower layer of soap solution is now run off, and the ethereal solution washed several times with cold water, which is drained entirely away. Finally the ethereal solution is run into a dry weighed flask, the ether evaporated off, and the resin oil dried at 221° F. and weighed.

The best laboratory tests for linseed oil are the refractive index, that is, for linseed oil 1·4835 at 15° C., and the iodine equivalent 170 to 188

For the determination of the iodine absorption of an oil by Hübl's test, the following re-agents are required:—(*a*) A solution of mercuric chloride in absolute alcohol (30 grammes in 500 c.c.). (*b*) A solution of iodine in absolute alcohol (25 grammes in 500 c.c.). (*c*) A decinormal solution of sodium thiosulphate, 1 c.c. = ·0127 gramme iodine. (*d*) A 20 per cent. solution of potassium iodide. (*e*) Chloroform. (*f*) Starch solution. 0·2 to 0·5 gramme of the oil is weighed into a clean dry flask, 10 c.c. of chloroform is added, and also 30 c.c. of Hübl's solution (made by previously mixing (*a*) and (*b*) solutions in equal measures); the flask is closely stoppered and allowed to stand in the dark for three hours. At the same time 10 c.c. of chloroform and 30 c.c. of Hübl's solution are placed in another flask and allowed to stand for the same length of time, but without the addition of any oil. After three hours 10 c.c. potassium iodide solution is added to each, then 20 c.c. water, and they are titrated with the thiosulphate solution, using starch as indicator, until the solutions become colourless. The number of c.c.'s required for the blank test minus the number of c.c.'s required for that with the oil multiplied by ·0127, gives the amount of iodine required for the oil, and this is then calculated on 100 pt. of oil, being known as the iodine equivalent or iodine value.

Linseed oil which has been boiled three times is sometimes called burnt linseed oil. It is darker than the other oils, and is used by litho printers, as it does not spread out on paper.

The discussion of the properties and preparation of linseed oil is now fairly complete, and other paint vehicles can be considered.

Turpentine is an oleo-resin secreted in various ways by pines, firs, spruces, and other members of the great group *Coniferæ;* and also by one or two species of the genus *Pistacia.* The crude material is collected from the trees in the form of a more or less slimy gum. This is taken to a distillery, where it is placed in a large cauldron and heat applied to slightly above melting-point of the material. Tepid water is allowed to run over the face of the resin as it becomes hotter and hotter. Eventually large quantities of spirits of turpentine and water distil over. By allowing the whole to stand for a short time the water

settles and the pure "oil" or "spirits" is run off into barrels ready for export.

Oil of turpentine, spirit of turpentine, and ordinary or common turpentine are all the same thing. Crude turpentine is turpentine as it is derived direct from the pine trees. Oil of turpentine really means the essential or volatile oil of turpentine after distillation, and must not be classed with the ordinary kinds of oils, such as olive oil, etc., which are non-volatile, and have a different composition altogether. There is an oil of turpentine known as fat oil of turpentine, but this is simply ordinary turpentine that has been exposed to air for some time and has become thickened or partly resinified by oxidation.

The methods of collecting turpentine differ greatly, and are to a large extent controlled by the nature and position of the secretion in the tree. Broadly speaking, some trees secrete the resin only in the bark—*Pistacia* and *Abies*—others in the sapwood—*Pinus palustris* and *maritima*—while the larch is said to yield its supply from the heartwood alone.

The principal supply of turpentine comes from the United States, and is obtained by "orcharding" or "farming" in the pine districts, and "boxing" the trees; by "boxing" is meant the cutting of cavities in the trunks near the ground to form a box of about one quart capacity. The season for getting the gum is from March to September, and from one to four boxes are cut in each tree according to its size. The "orchards" are mostly confined to areas covered by the "longleaf pine," better known, perhaps, as the Georgia pitch pine—*Pinus palustris*, Mills, or *Pinus australis*, Michaux, which are synonymous, and not *Pinus resinosa* as some books state. Notwithstanding its specific name *resinosa* (resinous), very little, if any, of the commercial resin or turpentine comes from this tree.

The pitch-pine trees are worked for several seasons in succession, but the quality of the resin deteriorates more and more after the first year (or, as it is locally termed, the "virgin dip"). Sixteen barrels of crude gum yield about 80 gal. of turpentine, and the residue of distillation produces about ten barrels of the ordinary resin of commerce, but the yield becomes less, in proportion to the bulk of crude material, after the first year, and so on until the

resin becomes so dark and poor, and the turps so little, that after working the trees, which usually takes from four to seven years, the orchard is abandoned or handed over to the lumbermen, and the farmer migrates to a new district.

The turpentine season covers about thirty-two weeks. During this time each tree is "dipped" for resin eight or ten times. About once every week or nine days, according to the round, the hackers visit the trees, and, cutting away a chip or two at the top of the cavity or box, re-expose the ends of the resin ducts. This is essential, as incrustations of solid resin occur on the face of the box and clog up the ends of the resin ducts, thus preventing the flow. Once or twice a year the whole face of the box is scraped and all hard resin taken away and distilled. Needless to say, this is of very poor quality. It is locally known as "hard scrape."

The Bordeaux turpentine is afforded by much younger trees than those from which the American turpentine is obtained, and is procured by scoring or blazing the trees in long vertical stripes, but, in contrast to the American method, these stripes do not penetrate far into the tree—through the bark and about ½ in. into the sapwood. The stripe is about 4 in. wide throughout its length, and, while at first very short—only 1 in. or 2 in.—is gradually lengthened upwards as the season advances. A receptacle, almost like a flower-pot, is placed and fastened against the stripe to receive the exuded turpentine. This is emptied from time to time. As a rule, only one stripe on each tree is worked at a time, more than this being likely to result in permanent injury to the tree. But if the plantation should require thinning, then certain of the trees are selected, have several stripes made on them at the same time, and the trees are allowed to bleed to death. They are afterwards cut down. With careful management a tree may be bled, at the rate of one stripe a year, for twenty or thirty years. This stripe method is also much practised in India in connection with *Pinus longifolia*, Roxb.

Russian and Swedish turpentines are obtained in a somewhat similar manner, and also by modifications of the box method. As commercial articles their drying qualities are said to be poor, or at least not to be as good as American and French turpentines.

Venice turpentine is procured by boring auger holes into the bases of larch trees (*Larix europæa*, D.C., formerly called *Pinus larix*, L.), each hole having a slight declination towards the centre of the tree. In this the turpentine collects, and is taken away periodically.

Strasburg turpentine is obtained from the silver fir (*Abies pectinata*, D.C.), and is collected principally in the month of August by peasantry in the Strasburg district. The resin-bearing habit of the tree is identical with that of the balsam fir. The method of collecting is also the same, and is described below.

Canada balsam, balm of fir, and balm of Gilead are names applied to the resinous product of the balsam fir (*Abies balsamea*, Mills). The turpentine is secreted by the tree in little vesicles or blisters which occur just underneath the cuticle of the outer bark. These blisters contain from a drop or two to a teaspoonful of beautifully clear, viscid, and colourless resin. The usual method of collecting it is by means of a can, which is provided with a long, sharp iron nozzle. The nozzle is placed against the bark just under the blister, and with a quick upward movement the blister is pierced and its contents looted, the resin running down the nozzle into the can. Small quantities of balsam may be collected in this way. The season lasts about two months, and the trees are worked about once in four years, or sometimes oftener. When brought in by the collectors, the resin is full of small black bark chips, bits of moss, etc., and requires to be clarified and strained before being placed on the market.

Chio or Chian turpentine is obtained from the *Pistacia terebinthus*, an evergreen tree indigenous to the shores of the Levant, being found particularly on the island of Scio or Khios, near Smyrna, in Asia Minor. Its leaves resemble, but are smaller than, those of the English ash tree. This tree was known to the ancients, and is even now often referred to as the "turpentine tree." The gums are obtained from the inner bark, where they are secreted in long fine tubes or "vessels." When incisions are made in the bark along the trunk and branches, the resin exudes and collects in oval drops around the edges of the cuts, or falls upon bundles of twigs or flat stones placed under the tree to receive it; it is afterwards elaborated in the

usual way. "Chio" probably took its name from Scio, and Chian from Chio, while the further term "China" may have originated in either.

The turpentine of commerce is obtained from three other important sources. The first is the "black," or Austrian pine, *Pinus laricio* var. *austriaca*, which is tapped largely in lower Austria, France, and Corsica. The resin of this tree is noted, and is said to contain a higher percentage of spirits than the resin of any other known species ; 100 lb. of resin yields 14 lb. to 29 lb. of spirits and 60 lb. of resin. More trees of this species are being farmed than any other in Europe. "Hungarian turpentine," so called, is obtained from pine trees on the Carpathian mountains. The particular species is *Pinus pumilio*, and the turpentine is believed to be obtained by boiling the young shoots. The "spruce turpentine" comes from the Norway spruce, *Picea excelsa*. Trees are farmed for the turpentine in Norway ; but the principal supply comes from the Black Forest in Germany. Here it is obtained by two methods: by removing a rather large piece of bark and then chipping the surface of the wood underneath, the exuded resin being scraped away from time to time, and also by making a V-shaped, narrow, vertical slit through the bark and into the sapwood. The slit is full length and depth from the beginning, but is widened each summer by being cut at the sides. The resin is hard and does not yield much spirits. "Burgundy pitch" is obtained from this species.

Spirits of turpentine, from whatever source supplied, though differing in some of their properties, invariably conform to the formula $C_{10}H_{16}$.

Strictly speaking, none of the above products from which turpentine is prepared can properly be called a gum, since it is not soluble in water like gum arabic. The true gums have the same composition as starch, *i.e.* $C_6H_{10}O_5$.

A general method of collecting and preparing turpentine is by making incisions through the bark, in the lower part of which the exudation collects, and is removed from time to time. In this state the turpentine is a honey-like mass, with a strong resinous odour ; it is called "gum-thus," Venice turpentine, etc. After a quantity of the turpentine has been gathered, it is heated usually in a very roughly made still, with a worm placed in a vessel of cold water.

By this means the product is separated into two constituents, a volatile oil which distils over, and a solid, yellow, glassy substance which remains in the retort; the volatile oil is terebine spirit, the pure spirits of turpentine, and the solid residue is the common resin or colophony.

Turpentine is a rather fragrant-smelling liquid, colourless when pure, but often more or less yellow. Its specific gravity varies between ·864 and ·869, and on heating it commences to boil at about 155° C., the greater portion distilling over below 172° C.; but there is always some residue, usually from ½ per cent. to 2 per cent. of non-volatile matter or resin. On exposure to air turpentine gradually becomes "fat," and, by oxidation, gradually changes into resin. It is a hydrocarbon, or, more properly speaking, a mixture of hydrocarbons which have the same compositions ($C_{10}H_{16}$), but different properties, perhaps the most noticeable being their action upon polarised light. American turpentine consists principally of dextro-pinene, and rotates a ray of polarised light to the right from + 8° to + 16°. French turpentine consists principally of læve-pinene, and rotates the ray to the left – 30°. Russian turpentine is composed mainly of sylvestrine, and rotates the ray to the right + 15° to + 23°. Turpentine evaporates readily at the ordinary temperature, and is inflammable, burning with a very smoky flame.

Terebine oil is produced by agitating the pure spirit of turpentine with a small quantity of concentrated sulphuric acid; this treatment is repeated several times, and the terebine is then washed with slightly alkaline water and distilled in a current of steam.

CHAPTER II.

COLOUR AND PIGMENTS.

The term pigment is applied to those coloured substances which, mixed with certain bases and vehicles, are used as paints. Pigments are often incorrectly called colours; as will be shown presently, colours are merely sensations which have no definite existence. Pigments are derived from various sources, many being mineral products, several are derived from vegetable sources, and a few are produced by animals. Some are spoken of as natural pigments, like the ochres, whilst others are classed as artificial; but, as a matter of fact, all pigments are more or less artificial, because in their natural state they are coarse and intractable, and require very careful grinding and elutriation (cleansing) before they are fit for use.

Pigments have generally a definite composition, and are more or less stable compounds. The inorganic pigments are coloured compounds of the different metals, usually of the heavier metals. The organic pigments are not so well defined, but they can all be placed in classes according to their composition. Useful as a chemical arrangement of pigments according to their composition might prove, it is still better for present purposes to describe them under the heads of their respective colours.

Before proceeding to describe the different pigments, however, a brief outline of the theory of colour will be given. Without entering into this subject too minutely, it may be examined sufficiently to obtain an idea of the origin of colour in coloured bodies. Colour has no real existence—that is, it is not inherent in any substance. Sir Isaac Newton discovered that the colour of any substance is due to the light which falls upon its surface. By removing the sources of light the body loses its colour; or by altering the nature of the light the colour may be modified. For instance, by passing white light through a yellow glass, colourless objects beneath appear yellow, and

blue objects appear green ; or if a red glass be used, colourless objects appear red, and blue objects appear purple ; other colours are also modified. It is also a well-known fact that such a light as gaslight, which is only a little yellower than daylight, produces a considerable change in the appearance of certain colours, rendering it difficult to match them by gaslight. These facts show that by modifying the light not only can colours be considerably altered, but that the appearance of colour may be produced in colourless substances.

If daylight, or what is termed white light, be analysed or split up, the origin of colour is soon made clear. The apparatus used for analysing white light consists of a glass prism (Fig. 17) which is made from a piece of flint glass, cut with three plane faces. The prism is mounted on a stand, so that it is capable of being moved to any position required. The room in which the experiment is conducted is darkened by means of a shutter, in which is cut a narrow slit through which a beam of light enters ; the prism being placed in its path, the beam is caught on one of the faces, and although it is capable of passing through the glass it is refracted out of its course, and at the same time split up into its constituents, which are various coloured lights.

The refracted beam forms a band of colours upon the screen (Fig. 18), and whilst the colours merge imperceptibly into each other, they may yet be fairly well defined into the six which Newton names—violet, blue, green, yellow, orange, and red. This band of colours when it is produced by splitting up the rays of the sun is known as the solar spectrum.

That white light is really composed of different coloured lights may be shown by bringing together again the coloured rays that have been separated by the prism, when they reproduce white. A similar result is obtained, though not so perfectly, by means of a revolving disc (Newton's disc), painted with the spectrum colours in the same proportions.

These different coloured lights appear to be merely sensations which act upon the optic nerves, and it is now almost universally supposed that light is really due to vibrations in a substance called the "luminiferous ether,

which substance is assumed to be everywhere present. These vibrations or waves are not all of the same length; from experiments it appears that the wave-length of the violet rays is the shortest, and by the prism they are refracted the most, while the red rays have the greatest wave-length and are least refracted.

The "undulatory theory" of light, as it is called, affords a good insight into the origin of colour. In the retina of the eye there are certain nerves which respond to the bounding of these waves, producing the sensation of light, and from the researches of Young and Helmholtz it appears certain that there are at least three separate sets of nerves each of which responds to light of a certain wave-length,

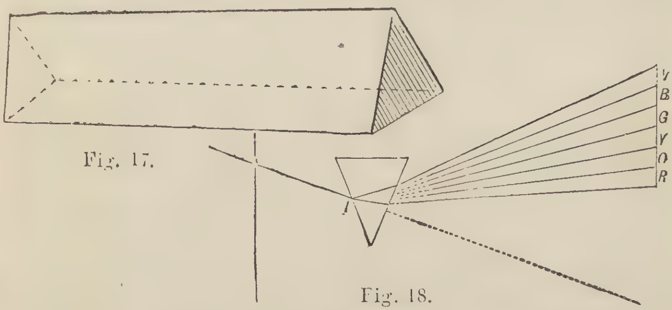


Fig. 17.—Glass Prism. Fig. 18.—Diagram of Spectrum.

producing, when excited by its means, a particular colour sensation. The three sets of nerves are capable of giving the sensations which are known as the colours red, green, and violet, respectively; and to the physicist these colours are undoubtedly the primary colours. When two sets of nerves vibrate, the sensations of the secondary colours are obtained, and when the three vibrate, either tertiary colours or the sensation of white is produced.

A part of the white light falling upon any surface is always reflected from the surface, but a portion also penetrates some distance into the body, and either becomes submerged or, after a number of reflections, returns again to the surface. When the light which penetrates is largely returned unaltered, the body appears white; when only a

portion is returned, the rest being submerged, the substance appears grey; and when all the light is submerged, we say that the body is black. In many cases, however, a portion of the rays are absorbed, only those rays of a certain wave-length being returned; the body then appears coloured. For instance, a red pigment absorbs all the rays of the spectrum except the red and a portion of the orange and yellow, when the prevailing tint of the body is red. A yellow substance absorbs all the rays with the exception of the yellow, a portion of the orange, and the green, but the prevailing tint is yellow.

Pigments, without exception, never have pure colours, because they allow to pass other tints besides the prevailing ones; they therefore only approximate to the pure colours of the spectrum. Moreover, they are less intense, owing to the amount of white light reflected from their surface diluting that which comes from the interior.

The painter's pigments are not direct central colours suitable to be placed at regular intervals upon the chromatic circle. Vermilion is a yellow tone of red; Indian red is purple in tone; light red is inclined to yellow, and is neutral in character. The nearest direct yellow is pale chrome. Prussian blue is a greenish kind of blue, and is a good colour for mixing green; ultramarine blue is a red blue, and makes, when mixed with yellow, a low form of green, on account of the red in the blue, which neutralises the green. Emerald green is a cold, strong green; cobalt is nearer to green than ultramarine. The ochres, siennas, and browns are all tertiary tints, and do not come within the scope of the chromatic circle. In none of the pigments is there direct central or pure colour, such as exists in the rays of light.

The luminosity of a pigment has reference to the amount of light which it reflects to the eye; its hue refers, not to the prevailing tint, but rather to that to which it inclines. For instance, yellow may be of an orange or greenish hue, according to the presence of orange or green rays accompanying the yellow. The tones of a colour are produced either by admixture with white, when they are known as tints; or with black, forming shades; or with grey, forming neutral tints.

Pigments do not retain their brilliancy unimpaired, and

their permanency is affected by many considerations, of which only a summary can be given here. Pigments may be tabulated as follow: (1) Those which are affected by light and normal atmosphere; (2) those affected by an atmosphere containing sulphuretted hydrogen; (3) those which suffer change by admixture with white-lead or other lead compounds; (4) those which are decomposed by mixture with ochre or other ferruginous substances; (5) those which withstand the action of light, of atmospheric oxygen and moisture, and of sulphuretted hydrogen, and which may safely be mixed with compounds of lead and iron.

Manufacturers' catalogues show a list of more than 150 different pigments, but the following list is all or more than an artist needs, and may be classed under table (5) of the above paragraph: Blacks—ivory black, blue black, and lampblack. Blues—French blue, permanent blue, cobalt, and cerulean blue. (Prussian blue is moderately permanent, being most durable when painting in deep tones, and though it may slightly fade in light, it regains its colour in the dark; also Antwerp blue is somewhat similar to Prussian blue, with less depth and less permanency.) Browns—madder brown, Rubens madder, umber, Verona brown, Vandyke brown, Caledonian brown, and sepia. Greens—oxide of chromium, viridian, and terre vert. Orange—burnt sienna and cadmium orange. Reds—vermilion, light red, Venetian red, Indian red, rose madder, and alizarin crimson. Yellows—aureolin, cadmium yellow, lemon yellow, raw sienna, yellow ochre. In addition to the above five tables, the action of the oil medium and the priming on the canvas should be considered.

Much attention is given in succeeding chapters to the methods of testing pigments by simple chemical reaction and by qualitative analysis. These tests, however, are not recommended unless the worker has had some experience with chemicals. Ordinarily, the easiest method of determining the strength and purity of pigments is to add, say, 5 per cent. of the colour to paste white-lead, and to treat a sample of known purity in a similar manner, and place the tints side by side. That possessing the deeper tint is evidently the stronger and better colour.

CHAPTER III.

WHITE PIGMENTS.

White-lead is by far the most valuable pigment used by the painter, its excellent body and covering properties, and its great durability, rendering it an excellent priming for all kinds of work, especially on wood, of which it is a valuable preservative. It also forms the basis of most tints and shades, and in application it works far more easily than most other pigments, and covers much better.

White-lead was first obtained, in small quantities, as a native carbonate of lead, and was named by the Romans "ceruse." In the third or fourth century B.C. artificial white-lead was produced by treating the native blue-lead with vinegar. A similar process was employed in Holland several hundred years ago; and the old Dutch method, with certain modifications, is still extensively followed. Many quicker methods have been adopted, but in none does the product excel that of the old Dutch or stack process.

This pigment is distinguished from all others by the ease with which it mixes with oil, and by forming a paint which readily flows from the brush. Its great disadvantage, however, is its poisonous character, which affects not only those engaged in its manufacture, but also those who are much occupied in applying it.

White-lead is a basic carbonate of lead, and is represented by the formula $2PbCO_3,PbH_2O_2$. It has far greater body and covering power than any other pigment, and consists of lead carbonate 68·95 per cent. and lead hydroxide 31·05. The carbonate is the material that imparts to white-lead its excellent body and colour, whilst the hydroxide in its composition causes the white-lead to combine chemically with the oil in a most perfect manner, thus giving the pigment its excellent covering properties.

The various processes of manufacturing white-lead are grouped under five heads, namely—(1) Stack method; (2) chamber methods; (3) precipitation processes based on

the action of carbonic acid gas on various lead salts; (4) precipitation methods based on the action of alkaline carbonates on various lead salts; (5) miscellaneous and obsolete methods, chiefly of historical interest.

The most common process, known as the Dutch process, was elaborated about four hundred years ago, and has been but slightly modified. In this method the white-lead is formed by the action of vinegar or dilute acetic acid and carbonic acid upon metallic lead.

The lead used for the purpose is sheet lead, which is cut up and rolled into spirals (Fig. 19). Each spiral, or coil, is placed in an earthenware pot, resting upon three

Fig. 19.

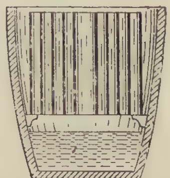


Fig. 20.

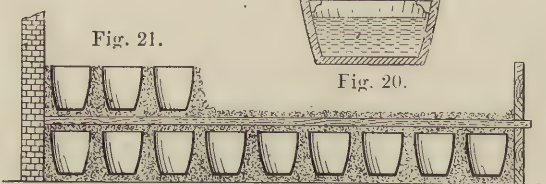


Fig. 21.

Fig. 19.—Coil of Sheet Lead. Fig. 20.—Corroding Pot.
Fig. 21.—White-lead Chamber.

projections in the interior (Fig. 20). Previous to the introduction of the coil, the pot is about one-fourth filled with vinegar or dilute acetic acid, and after the introduction of the coil the pot is covered either with a lid or with a plate of lead. A considerable number of these pots, having been charged, is arranged in the following manner:—A temporary wooden structure is often employed, made by placing four planks of wood, set edgewise, upon the floor; in this square is spread a layer of fresh horse-dung or spent tan-bark, upon which the pots are placed and well packed in with the dung or bark, until they are entirely covered up (Fig. 21). A platform of planks is next put down, which rests upon those set edgewise on the floor, and upon this platform four other planks

are set, then the layer of pots and dung or bark, and this order is continued until the wooden structure is entirely filled. This is now left to itself, and in a short time, owing to fermentation taking place in the dung or spent bark, the whole becomes heated.

The warmth imparted to the pots causes evaporation of the acetic acid in the vinegar, which immediately attacks the lead spirals, with the formation first of acetate of lead, then of basic acetate; finally, by the action of carbonic acid liberated from the dung, this becomes changed to basic carbonate, or white-lead. The operation is progressive until the fermentation is over, when the pile gradually cools down. After about five weeks the boards are removed, the pots taken out, and the structure swept clean for the next operation. The coils of corroded lead are taken out and passed through a machine, which, having corrugated rollers, removes the white lead from the unaltered cores of metal. The latter are separated by a sieve, through which the white-lead falls into boxes. The white-lead is thoroughly ground, washed, and finally drained and dried.

The Gustav Bischof process of making white-lead, as compared with the old Dutch process, is comparatively innocuous, and the conversion of the metallic lead into the commercial white-lead paste takes only forty-eight hours, as compared with three or four months by the old process. The metallic lead is first converted into litharge, in furnaces to which an induced current of air is supplied by means of steam jets, the pig lead being oxidised by the action of the air. The furnaces are heated by producer gas. The litharge is passed through an air-tight disintegrator, in which it is pulverised, the powdered litharge being afterwards carried forward into a closed dust collector. From thence the powdered litharge is conducted into air-tight cylinders. Here the litharge, which is a mixture of various oxides, some of which cannot otherwise be converted into white-lead, is reduced to a practically uniform sub-oxide by the aid of water gas at a temperature of about 572° F., and is moistened with water in hydrate mixers. Here the sub-oxide absorbs atmospheric oxygen and combines chemically with the water, forming a practically uniform hydrated oxide of lead. The hydrated

oxide is then charged into gas-tight carbonators, in which it is agitated by stirrers in a weak solution of acetic acid. Carbonic acid gas is passed into the carbonators under pressure until the desired uniform degree of carbonation has been attained, which is impossible in the case of lead made by the Dutch stack process. The white-lead sludge thus produced is forced by compressed air from the carbonators to filter presses, where it is pressed into cakes, these being then mixed with oil, which combines with the white-lead and causes a separation of the surplus water in the pressed cake. The paste thus formed is passed through an ordinary mill, leaving it as the ground white-lead of commerce.

Analyses of the Bischof product show that while it is identical in chemical composition with the ordinary white-lead of commerce, it appears to have more covering power, presumably owing to some difference in its physical condition. As regards the health of the workmen employed, it may be noted that little or no dust is set free in the course of its manufacture, the grinding mills, elevators, etc., being all dust-proof; moreover, drying and packing the white-lead powder—the most dangerous parts of the old process—are altogether avoided.

Numbers of patents have been taken out for preparing white lead by other processes which would shorten the operation. Many of these are for producing white-lead by precipitating the basic acetate with carbonic acid—processes which can be easily carried out; but, unfortunately, their product has not the covering power of white-lead formed by corrosion, but is crystalline and more transparent. Space cannot be given to describe further the different processes invented, especially as most of them have not been commercially successful.

White-lead is offered for sale in two forms—as dry powder, and as a stiff paste in oil. The latter form is principally used by the painter. To prepare it in this manner it is placed in a mixing mill driven by steam power, and 9 per cent. of refined linseed oil added, the product being afterwards passed between heavy granite rollers or levigating stones in order to ensure perfect fineness.

Where high-class work is to be done, as in flatting

panels, and in building up work for enamelling, it is essential that the white-lead shall be very fine, as on this quality the finish of the work depends. The simplest method of determining the fineness and density of white-lead is to place a small sample of the lead on a piece of glass with a little oil, and rub it on the glass until an almost transparent layer is formed, when any grit or any small particles of lead may easily be seen or felt on the palette knife. The density may also be checked by adding a small quantity of black to two samples of lead of equal weight; the deeper shade will indicate the lesser density.

The adulteration of white-lead was practised to a considerable extent before the Merchandise Marks Act was introduced, but now a special committee is empowered to analyse suspected samples of white-lead, and to take action against offenders adulterating or reducing it.

The chief adulterant in the manufacture of white-lead is barytes, whilst small quantities of china clay and gypsum are sometimes used. The degree of purity may be ascertained by a variety of simple tests, a few of which may be here given: (1) Take on a palette knife, scraper, or ladle, a small quantity of the suspected sample, and place it over the fire or over a gas jet. If the lead is pure, it will quickly turn into blue-lead, any residue representing the adulterant. With regard to how much metallic lead would be obtained in testing 1 lb. of pure white-lead, of course, the whole pound would not be tested; from 1 gr. to 20 gr., according to the method of analysis pursued, would be the quantity taken. Calculating from the amount yielded in the analysis to what 1 lb. of pure white-lead would yield if submitted to the same treatment, the quantity of metallic lead produced would be approximately $12\frac{3}{4}$ oz.

(2) Place the white-lead in a small cavity of a piece of charcoal, then direct the flame of a blow-lamp on it, until if pure, it will be entirely converted into blue-lead, any residue remaining being the adulterant.

(3) A very easy and trustworthy test for white-lead is to dissolve the lead in dilute nitric acid, one part acid to two parts water. If the lead is pure, it will entirely dissolve, only the oil remaining on the surface of the vessel. Should there be any insoluble residue, this will represent the adulterant.

Pure or genuine white-lead of a good quality is stringy and firm when handled, whilst the reduced or common lead is short and crumbly.

A yet simpler method for detecting adulterated white-lead is by comparing the cubical contents of each package. Pure white-lead should weigh about 400 lb. per cubic foot. The addition of barytes or whiting will increase the bulk. This method is only trustworthy when the lead contains above 25 per cent. of barytes, when the increase in bulk may easily be noticed by those accustomed to handling the material.

White-lead endures well under exposure to the hot sun, and to the influence of the normal atmosphere; but sulphuretted hydrogen rapidly discolours it, black sulphide of lead being formed. Acids and alkalies also act upon it. White-lead may be mixed with nearly all pigments, except those containing sulphur; ultramarine, and cadmium yellow, for instance, soon cause the resulting colours or tints to turn black. When white-lead is used on damp surfaces and kept from the light, it rapidly discolours, but is often restored on exposure to sunlight. A protective coat of varnish is useful in averting some of the disadvantages just enumerated.

The pigment is not recommended as a primary coat for ironwork, as, unlike red-lead, it does not possess the elasticity required in order to allow for expansion and contraction of the metal surface it covers. It may, however, be used with advantage for the finishing coats on ironwork.

Flake white, used by artists, is a very pure white, not likely to discolour; it is on this account generally used as a finish over previous coats of white-lead. It is prepared by grinding pure English white-lead in refined poppyseed oil. The Cremnitz white also used by artists is prepared in a similar way by grinding white-lead and pure zinc oxide or zinc white in refined linseed oil. The proportions are usually white-lead 14 lb., refined poppyseed oil 1 pt.; zinc white 14 lb., refined linseed oil 2 pt. These pigments are ground very fine through granite rollers, and are then placed in collapsible lead tubes ready for sale.

"Glasgow" white, zinc white, Orr's white enamel (or Charlton white), Griffith's patent zinc white, and Freeman's white, have one advantage over white-lead—that is, they

are not so readily acted upon by sulphuretted hydrogen; therefore, if used in towns where foul gases are likely to be evolved, they do not so soon blacken; some of the substitutes do not change colour at all in situations where white-lead will rapidly become discoloured. "Glasgow" white and Freeman's white darken but slowly, while zinc white, Orr's white, and Griffith's white are not affected. White-lead has greater body and covering power than any of the other white pigments, none of the substitutes being quite equal to it in this respect, whilst some are rather poor in these qualities. Those substitutes containing sulphide of zinc, such as Orr's and Griffith's white, discolour pigments containing copper or lead, owing to the formation of the sulphides of those metals. This defect is not shared by white-lead, though white-lead is itself discoloured by other pigments, as has been explained.

A further advantage of the lead substitutes is that they are far from being so poisonous as the usual carbonate of lead.

Zinc white, or oxide of zinc, ZnO, also known as Chinese white, is used on an extensive scale, chiefly for the preparation of enamels and distempers. It is of a pure white colour, and is permanent in both oil and water. Its only defect is want of body or covering power as compared with white-lead. It has a much less specific gravity than white-lead, and thus requires more oil to render it of a workable consistency, and becomes somewhat translucent. It will mix well together with any other pigments without deterioration, and is very much used where any white surface is to be prepared, as upon interior decorative enamelled work, and, on account of its non-poisonous properties, is preferred for this and for many other classes of work. Zinc white may easily be distinguished from other white pigments by its being entirely soluble in dilute sulphuric acid without effervescence.

Zinc white consists of practically pure oxide of zinc —ZnO. Occasionally, however, the name is taken to include sulphide of zinc white and lithopone, which is a combination of zinc sulphide and barium sulphate. The ZnO is prepared by subliming metallic zinc and allowing the vapour to burn in air, the fumes produced being afterwards condensed. The sublimation of the zinc is performed in

retorts made of fireclay in the form shown by Fig. 22. These are set in series back to back in a reverberatory furnace (Fig. 23). The mouths of the retorts A open into an air-chamber B at the front of the furnace, which is supplied through the flues C with air heated to a high temperature by the waste heat of the furnace. A bent pipe D at the top of the air-chamber connects it with the condensers E. The condensers are rectangular chambers connected in series of four by openings alternately top and bottom, these openings being covered with wire gauze; the bottoms of the chambers are prolonged into hopper shapes as at

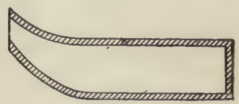
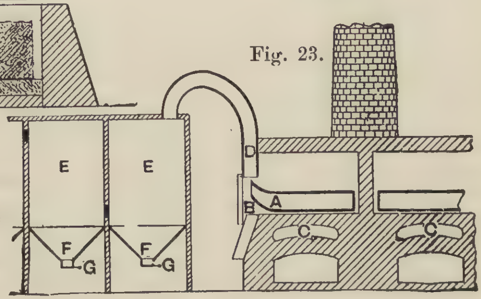


Fig. 22.

Fig. 23.



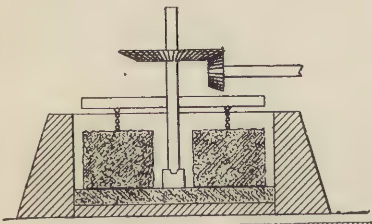


Fig. 24.

Fig. 22.—Zinc White Retort.
Fig. 23.—Zinc White Furnace.
Fig. 24.—Flat Stone Grinding Mill.

F, and provided with slides for opening and closing the apertures G.

The retorts are first raised to a red heat, and then a bar or two of metallic zinc is placed in each retort. The metal quickly melts and volatilises, the vapour taking fire in the air-chamber, where it meets the current of hot air; the fume is then carried by the tube D into the first condenser, from which it passes into the others; the zinc oxide is condensed on the walls of the chambers and in the hoppers. From time to time the condensed oxide is swept down and delivered through the hoppers into barrels ready for sale. The content of the first chamber is generally of a bad colour, owing to contamination with

metallic zinc, but the remaining chambers contain a pure white product.

Zinc white being merely the oxide of zinc ZnO, the reaction which occurs in its manufacture is one of the simplest—that is, the direct union of the two elements zinc and oxygen. This reaction is shown in the following manner:—

$$\underset{\text{Zinc.}}{Zn.} + \underset{\text{Oxygen.}}{O} = \underset{\text{Zinc oxide.}}{ZnO.}$$

Zinc white is a beautiful white product, having a moderate covering power. It is used instead of white-lead in places where sulphuretted hydrogen exists, as it is not acted upon by that gas. Zinc sulphide is also used to some extent as a white pigment. The pigments known as Orr's zinc white, or Charlton white, and Griffith's zinc white, contain both oxide and sulphide of zinc, as well as barium sulphate.

Charlton white and lithopone are prepared by calcination and precipitation, and are chiefly composed of zinc sulphide, zinc oxide, and barium sulphate. The composition of the first-named pigment may vary somewhat according to the proportion of ingredients used. These whites are extensively used for all classes of work, both interior and exterior, and their excellent body and covering power render them efficient substitutes for white-lead, over which they possess the advantages that they are not affected by sulphurous gases, and are non-poisonous. They mix well with most pigments, excepting those containing copper, as Brunswick, emerald, and mineral greens and verditers.

Glasgow white is a sulphate of lead ($PbSO_4$) produced direct from the native lead sulphide called galena by heating it in a furnace burning coke; the sulphate of lead formed is in the character of a fume, which is condensed and becomes an excellent white product. Though there are several methods of producing this pigment, the process as carried on at Glasgow is the method originally patented by Mr. Hannay. Glasgow white is a very fine pigment, of good body; it is likely to supersede the true white-lead, at least to some extent, because, being non-poisonous, it is not injurious to the workpeople engaged in manufacturing it or to those using it, a property which, it is well known, cannot be claimed for white-lead.

The white pigment known by the name of barytes is the sulphate of barium $BaSO_4$, which is produced to some extent artificially, though the greater part of that used in paint making is the natural mineral ground and washed or otherwise purified. Barytes occurs in Derbyshire, Cumberland, Devonshire, Cornwall, etc., and in Ireland, as also abroad. The mineral is broken into small lumps, from which the larger impurities are removed by hand; the barytes is then crushed to powder in an edge-runner mill, and then further comminuted in a mill similar to that shown in Fig. 24, which consists of four large blocks of granite, two of which are shown, revolving on a flat stone

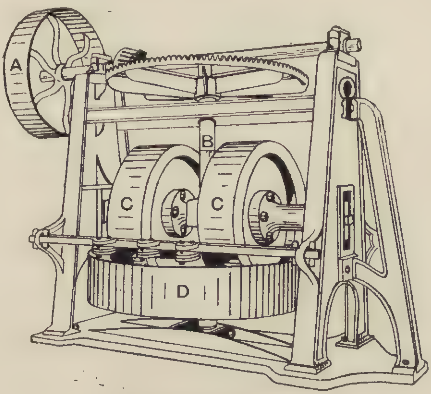


Fig. 25.—Edge-runner.

bed. During the grinding a constant stream of water is kept running through this mill, which carries off the finer particles of barytes, and, after settlement in a series of large tanks, these separate out, forming layers on the bottoms of the tanks from which the water is easily drained, the product then being dug out and dried. The finer kinds of barytes are obtained from the tanks farthest away from the mill.

The barytes produced as above described is more or less coloured by impurities which are not removed during the grinding. If a pure white product is required, the barytes is placed in a tank in which it is treated with acids, and

steamed, whereby the impurities are dissolved out; the product is then again washed and dried.

Barytes is rarely, if ever, used alone as a pigment; it is, however, largely used for mixing with other pigments, either for producing tints or for the purpose of adulteration; the pigment is very transparent, but it has one good quality—that of permanency—hence it has acquired the name of permanent white, or blanc fixe.

Gypsum is a mineral found in Derby, Nottinghamshire, Staffordshire, and Sussex, as well as on the Continent and elsewhere. It is the sulphate of calcium, ground the same way as barytes, and chiefly used by paper-stainers.

Kaolin, or China clay, another natural white, is a true clay or silicate of alumina, and occurs as a natural product of the decomposition of felspar—water removing the potash and part of the silica—in Cornwall, near Limoges in France, in Saxony, and in China and Japan. It is raised from the mines by injecting water, from which, after it has been pumped up again, the kaolin is deposited. The pigment is used only in admixture, as it is transparent.

Whiting, Spanish white, or Paris white, is produced from chalk—a soft powdery rock occurring largely in the south of England and in Yorkshire, forming the beautiful white cliffs so much admired. The beds, in some instances, are as much as 1,200 ft. in thickness. Chalk is one of the forms of calcium carbonate—carbonate of lime—($CaCO_3$), and though occurring in very large tracts, its origin may be traced to certain minute organisms, known as foraminifera, which occur in the sea, from the waters of which they absorb sufficient lime to build up their tiny shells, which are quite invisible to the naked eye, the rock appearing as an extremely fine white powdery mass.

Whiting is prepared from chalk by grinding it to a smooth paste with water in an edge-runner mill, and then transferring it to a flat stone mill (Fig. 22), in which it is more thoroughly ground and submitted to a stream of water, the finer particles of chalk passing with the water into tanks, in which it is allowed to subside while the water flows away. After draining, the whiting is dug out, allowed to dry under cover as far as possible at the ordinary temperature, and afterwards thoroughly dried in a room whose floor is kept heated by a coil of steam pipes.

Whiting is a smooth white powder ; mixed with oil it becomes quite transparent, and for this reason it is of no value as an oil paint ; it is, however, largely used in distemper painting, either alone or coloured by other pigments ; it is also the basis of putty, and it is used to some extent as an adulterating agent.

Whiting is nearly pure carbonate of lime, containing only traces of silica, alumina, etc. It very often contains a small percentage of alkaline matter in its composition, this being caused by the overheating of the stones, producing quicklime, which quickly attacks such colours as chrome yellows, Prussian blue, and Brunswick greens, whilst most of the other pigments are not affected in the least.

The edge-runner and the levigating machine have been referred to more than once in this chapter. They

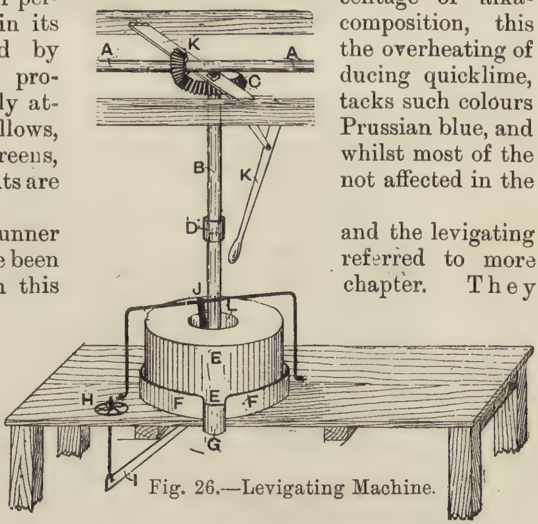


Fig. 26.—Levigating Machine.

now are illustrated by Figs. 25 and 26. In the former, A indicates the driving wheel or pulley ; B, the vertical indicates the driving wheel or pulley ; B, perpendicular shaft ; C, C, pair of stones, each weighing 15 cwt. ; D, pan for containing the pigment, which is prevented from adhering to the sides by a scraper. In Fig. 26, which represents the levigating machine, A shows the horizontal shaft driving the vertical shaft B by means of a bevel gearing C ; D, socket on the vertical shaft ; E E, the grinding stones, are made from Herefordshire stone, and placed one above the other, each being "dressed" with furrows, so as to conduct the pigment outwards ; F F, a sheet-iron

rim placed round the stones; G, spout to carry the pigment from the stones into a receiving tub placed underneath; H, wheel to lift the top stone, which runs on a pivot resting on the bar I, this being the means of regulating the grinding; J, a scraper fastened to the cross-bar to keep the pigment from adhering to the sides of the stone;

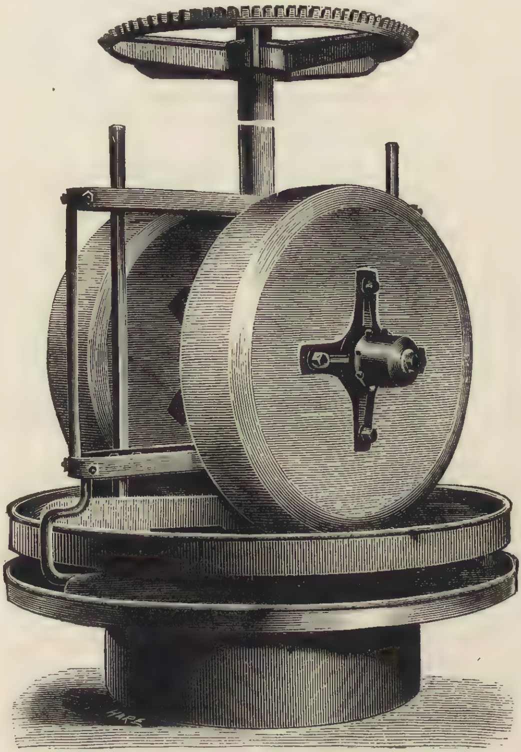


Fig. 27.—Edge-runner.

K K, an arrangement for throwing stones out of gear by sliding the vertical bevel wheel; L, the hole or hopper.

A typical edge-runner, made by Messrs. Rose, Downs, and Thompson, is shown by Fig. 27.

CHAPTER IV.

BLUE PIGMENTS.

Blue pigments exist in great variety, and most of them are remarkable for permanency. Those most commonly used are Prussian, Brunswick, ultramarine, smalts, lime, verditer, cobalt, and several compounds of these, sold under many different names. Others, again, are of but slight commercial value, owing either to their want of permanency or to the prohibitive expense of preparation.

Prussian blue is known also as Chinese, Paris, and Berlin blue, and modifications have also their particular names. This pigment was discovered in the early part of last century by a German chemist while he was compounding for another purpose the crude materials that are now used (with additions) in its manufacture.

In the trade the finer qualities of Prussian blue are sold as Chinese blue, that is, the portion of the pigment having a peculiar bloom or lustre. Paris blue is any Prussian blue with a violet tint. Brunswick blue is the same pigment, except that it contains barytes or gypsum added at the time of precipitation.

Prussian blue was originally prepared by calcining a mixture of nitre and cream of tartar, and then roasting the residue mixed with dried blood; the product, dissolved in water, was added to a solution containing alum and ferrous sulphate, and the blue precipitate thus produced was treated with hydrochloric acid.

Since the two salts of potash—the ferrocyanide and ferricyanide—have become commercial articles, these have taken the place of the necessarily impure roasted product formed from nitre, cream of tartar, and dried blood.

Under the name of Prussian blue are now grouped three distinct blue products: (1) Soluble Prussian blue, or potassium ferric ferrocyanide ($K_2Fe_2(FeC_6N_6)_2$); (2) insoluble Prussian blue, or Williamson's blue ($Fe_7(CN)_{18}$); and (3) Turnbull's blue, or ferrous ferricyanide ($Fe_5(CN)_{12}$).

Soluble Prussian blue is formed by adding a solution of potassium ferrocyanide ($K_4Fe(CN)_6$) to a solution of ferric chloride (Fe_2Cl_6) and washing the precipitate with water until the filtrate appears blue; the blue left on the filter is then dried, and is quite soluble in water. This was at one time thought to be a ferric ferrocyanide, but, as shown above, it contains potassium. It has no use as a pigment, the Prussian blue in most common use being the insoluble kind, No. 2 in the previous paragraph. However, there is a soluble deep blue in use made by adding ferrous sulphate to red prussiate of potash, and precipitating by adding acid (see p. 62).

There are several methods of manufacturing Prussian blue, the following being a common one:—A solution of copperas (ferrous sulphate, $FeSO_4$) is made with cold water in a tub; in another tub is prepared a solution of yellow prussiate (potassium ferrocyanide, $K_4Fe(CN)_6$), the two solutions are then run into the precipitating tub, when "white paste," a bluish-white precipitate of potassium ferrous ferrocyanide ($K_4Fe_4(CN)_{12}$) immediately separates. The clear liquid is drained off, and the precipitate washed as rapidly as possible with several changes of water. The precipitate is afterwards treated with a solution of bleaching powder (calcium hypochlorite $CaOCl_2$) and hydrochloric acid (HCl), whereby it is oxidised to ferric ferrocyanide, or Prussian blue ($Fe_7(CN)_{18}$). After again washing the precipitate with several changes of water, it is filter pressed, and dried in the dark at a temperature of about 130° F.

Another method is identical with this as far as the production of the precipitated "white paste." Then the upper liquid is syphoned off, and the precipitate heated in a boiler with oxidising agents, such as a mixture of bleaching powder and hydrochloric acid, or nitric acid (HNO_3). The colour of the precipitate changes to dark blue, and after standing some time the liquid is drained off and the blue run into the filter press and thoroughly pressed to get rid of the excess of water; the cakes of blue are then cut up and dried at a temperature of about 80°.

For certain purposes, as for paper staining, the blue is not dried, but is sent out in the form of a paste.

Alum is very often added during the above process,

and yields very good products, slightly paler than with copperas alone.

A manufacturer's recipe for Prussian blue is as follows:—56 lb. of green copperas and 56 lb. of yellow prussiate of potash are separately dissolved in water. One solution is added to the other, and the precipitate is oxidised with 28 lb. of sulphuric acid and 14 lb. of nitric acid. In order to obtain the blue of a good colour, good green copperas must be used, and the bluish-white precipitate obtained by mixing the solutions must not be oxidised by exposure to the air, but should be acted on at once by the acids. The blue is placed in a filter press, and then dried. Other proportions are: Yellow prussiate of potash, 56 lb.; green copperas (ferrous sulphate), 56 lb.; sulphuric acid, 8 lb.; chloride of lime, 8 lb.; hydrochloric acid, ½ pt.; water, 100 gal.

A few points in the manufacture of this pigment have yet to be referred to. As copperas is liable to go "rusty," it is necessary to add a proportion of either hydrochloric or sulphuric acid to the copperas solution to clear it and dissolve this oxide. The two solutions are then run together, as has been described, to yield a white precipitate technically known as the "white paste." This paste is absolutely white only in the absence of air, and in ordinary working is bluish in colour. The "white paste" is then washed and oxidised as already explained.

Common Prussian blues are usually oxidised in the air, and all such contain a proportion of ferric oxide, which darkens the shade. Though the process is simple, it is yet by no means easy to match a given shade, and it is even difficult to repeat a stock shade time after time. This is due to the sensitiveness of the blue to slight variations in the conditions of the manufacture. With the same white paste, and in the same conditions of temperature, etc., each oxidising agent gives its own shade; yet by merely varying the conditions, any one oxidising agent will yield practically the whole range of shades. Hence the importance, in repeating any shade, of exactly reproducing the same physical conditions. In general, a white paste made from concentrated solutions yields bright blues of a reddish tone with little or no bronze; while blues obtained from a white paste made from dilute solutions are dark, rather greener, and more or less highly bronzed.

Oxidation at the boil brightens the shade, and gives the least bronze; and in the cold the reverse is obtained, and so on. Each little alteration in the make, even in the quantity made, has its effect on the finished colour.

Turnbull's blue is prepared in the same manner as the ordinary Prussian blue, but is not oxidised afterwards, and in place of the ferrocyanide or yellow prussiate of potash ($K_4Fe(CN)_6$), the ferricyanide or red prussiate ($K_3Fe(CN)_6$) is employed.

Antwerp, Brunswick, and Celestial blues differ from each other but slightly in composition. An addition of barytes ($BaSO_4$) or gypsum ($CaSO_4 2H_2O$) is made during the time of the precipitation, and these white materials serve to form different tints of blue according to the amount added. Some makers add other ingredients which are not essential.

It may be mentioned that Prussian blue is now produced on a large scale as a by-product of gas manufacture.

The blues known under the general term Prussian blues are rather peculiar compounds, because they contain iron not only as a base, but also iron in the acid part of the compound; they are derived from the two acids, hydroferrocyanic acid $H_4Fe(CN)_6$, and hydroferricyanic acid $H_3Fe(CN)_6$.

Prussian blues are extremely fine pigments, and though not entirely permanent on exposure to light, they are nearly so; they are not altered by exposure to foul air, and are useful both in water and oil, being somewhat transparent. They are quick driers. They may be mixed with most pigments, with the exception of those containing any alkali, as soda, potash, ammonia, or lime. They cannot be used in distempers for the walls of new buildings containing lime, whiting, etc., as the lime would change the blue into an oxide of iron of a dirty-brown colour.

The Prussian blues are used extensively for preparing the well-known Brunswick green, which is produced by adding in variable proportions the lead chromes (see Chapter VII., p. 88).

Soluble deep blue is much used by paint and colour grinders, as well as by ink manufacturers. It is made by dissolving 6 lb. of ferrous sulphate in warm water in an earthenware vessel, while in another vessel is dissolved

9 lb. of red prussiate of potash, the solutions being well stirred together and boiled for an hour and a half, then $2\frac{1}{2}$ lb. of sulphuric acid is added, and boiling is renewed for an hour and a half longer. The mass is then run into a vessel with a large volume of cold water stirred well, and allowed to precipitate. The clear water having been finally syphoned off, the pigment is filtered and dried. Care is taken to cover the surface of the vessel whilst adding the acid, as the vapour is injurious to health.

Ultramarine, a most beautiful blue pigment, will now be considered. It has been in use for a long period, and was obtained from the mineral lapis lazuli, which occurs sparingly in Siberia, Transylvania, Persia, Korea, China, etc. The lapis lazuli is crushed, heated in a furnace, and thrown into cold water, which facilitates its conversion into powder. It is then agitated with dilute acetic acid to remove all traces of carbonate of lime. The sediment is mixed into a paste with a resinous composition, and kneaded under water until all the colouring matter is extracted. The colouring matter having been allowed to settle, the clear water is syphoned off, and the precipitate strained, dried, and sold as pure ultramarine, at prices ranging from £2 to £6 per ounce. It therefore has but a very limited use, the commercial ultramarines being artificial products.

On analysis lapis lazuli is found to contain silica, alumina, soda, and sulphur; but the analyses that have been made of it are very variable, owing to the presence of more or less impurity which cannot be removed. The following are the analyses of natural ultramarine by Schultz and Gmelin respectively:—

	Schultz.	*Gmelin.*
Combined sulphur	3·16	0·188
Sulphuric acid	5·67	4·639
Silica	43·26	47·346
Alumina	20·22	22·000
Calcium carbonate	14·73	—
Calcium oxide	—	1·546
Soda	8·76	12·063
Oxide of Iron	4·20	—
Water and loss	—	12·218
	100·00	100·000

The extraction of the natural ultramarine, however, has now been almost entirely abandoned, the precious stone being used for the manufacture of costly inlaying and ornamental work.

Ultramarine obtained from lapis lazuli, it may be said, is the finest blue pigment in existence; the artificial varieties, when properly made, are also extremely good, but there are many different tints now on the market, some being a nearly pure blue, some greenish, and others violet. Ultramarine is quite permanent under the action of light, air, moisture, etc. It may be used in distemper, but acid vapours bleach it by removing the sulphur in the forms of sulphuretted hydrogen.

The constitution of commercial ultramarine is doubtful, but it is probably a silicate of alumina and soda combined with sulphide of sodium.

The two varieties of commercial ultramarine are known respectively as the soda and the sulphate ultramarine. The sulphate ultramarine is of a greenish blue, whilst the soda ultramarine is of a violet blue colour. The soda ultramarines are generally made in two qualities. The finest quality is used chiefly by lithographers, paper-makers, and calico printers. It is usually rich in silica, which renders it more highly proof than non-siliceous ultramarines against the action of alum solution. Ultramarine poor in silica is much used by paint-makers.

The materials used in the manufacture of ultramarine are kaolin, calcined sulphate of soda, carbonate of soda, sulphur, charcoal, resin, quartz, and kieselerde. Iron-free kaolin should contain silica and alumina in the proportion of 2 silica to 1 alumina for the manufacture of sulphate ultramarine, while the proportions for the soda ultramarines should be from 2 to 3 silica to 1 alumina. The following recipes will give an idea of the proportions for the sulphate ultramarine which is used in the Nuremberg process:—

SULPHATE ULTRAMARINE.

	Parts.
Kaolin (calculated as anhydrous matter)	100
Sulphate of soda (calcined)	83
Charcoal	17
Sulphur (powdered)	13

SODA ULTRAMARINE (PAINTERS').

	Parts.
Kaolin	100
Sodium carbonate	100
Charcoal	12
Sulphur (powdered)	60

SODA ULTRAMARINE RICH IN SILICA (PRINTERS').

	Parts.
Kaolin	90
Quartz	10
Kieselerde	10
Sodium carbonate	105
Sulphur	62
Charcoal	14
Colophony	3

The manufacture of the sulphate ultramarines usually requires two processes, namely, calcining and colouring. In the newer method of preparing ultramarine, the calcining and colouring are done in one process, which is chiefly used for making the soda ultramarines, and is generally known as the crucible method. The ingredients of the ultramarine are all thoroughly ground into a very fine state of division, mixed together, and then placed in crucibles of various sizes (usually about 7 in. by 5 in.), which are fitted with flat lids, plastered on with a preparation made from china clay. The plaster having been allowed to dry, the crucibles are placed in a furnace similar to a large oven. The sizes of the furnaces vary at different works. Some furnaces hold from 500 to 1,000 crucibles. The furnace doors, etc., are then plastered up, and the furnace is heated to a cherry-red for several hours, until the desired depth of colour is obtained. The furnace is then allowed to cool for several days, care being taken not to admit any air, otherwise the resulting colour of the finished ultramarine will be injuriously affected. The crucibles are then taken out of the furnace, and the crude ultramarine is emptied out and sorted.

At this stage the ultramarine has a somewhat ashy-blue colour, is mostly in lumps, and has in its composition much soluble sodium salts, which are removed by treatment with water and grinding in large edge-runner mills. The

blue mass is further ground in fresh water under flat levigating stones until the blue is absolutely fine, when it is further treated with more fresh water and the various grades of colour are separated. That which remains longest in suspension in the water is considered to be the finest in quality. It is seldom or never possible to find any two batches of ultramarine exactly alike in colour. The standard colours are usually made up by grinding and mixing various shades and batches until the desired colour is obtained.

By the older system of making ultramarine, employing two distinct processes—calcining and colouring—a mixture is made of kaolin or china clay, carbonate of soda, sulphate of soda, charcoal or coal, sulphur, and resin, and sometimes quartz, etc., in the proportions found best by practice, variations being made according to the kind of ultramarine specially desired. The mixture is placed in crucibles, which are stacked in tiers one above another in the furnace (Fig. 28), open in front, and with holes B B and C C in the hearth and roof of the furnace, through which the flames and hot gases pass from the fireplace A to the chimney D. When the furnace is filled with pots, the front E is bricked up, and the fire is started. The roasting of the mass being completed, the fire is quenched and the furnace allowed to cool down; the pots are then removed and the greenish material is thoroughly ground and washed, and then dried and heated either in a cylinder or a muffle furnace, somewhat similar to Fig. 29, but with a closed muffle in place of the open hearth B. Sulphur is projected upon it in small quantities at a time until the blue colour has fully developed; the ultramarine blue is then raked out, and subsequently thoroughly ground with water, and graded or separated into different qualities by a process of levigation carried on in tubs placed in series one above another, the fine particles being carried by the flowing water from one tub to the other, the finest quality separating in the last tub and others in the intermediate ones. In Fig. 29, A shows the fireplace, B the furnace bed, D the sight holes, and C the flues, the arrows showing the direction of the flames and hot gases.

Ultramarine should not be mixed with white-lead, yellow or orange chrome, mineral green, emerald green,

Prussian blue, Brunswick or Antwerp blues, or red-lead. It may be used, however, in lime colouring or in distemper, as alkalies have no deteriorating effect on it. The cheaper grades of ultramarine entirely supersede the once much used lime blue, and are now principally sold under the name of lime blues. The true lime blues are described on p. 68.

There are three blue pigments containing cobalt, Thenard's blue, smalt, and cœruleum.

Thenard's blue is prepared by mixing together solutions of alum and cobalt nitrate ; the addition to this solution of sodium carbonate causes a pale pink precipitate, which,

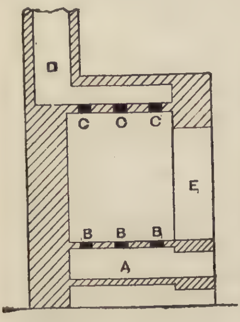


Fig. 28.

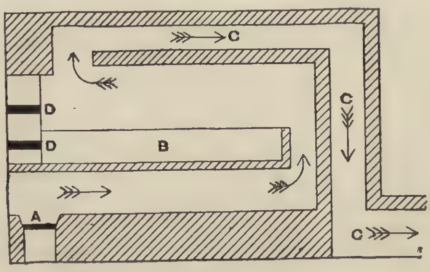


Fig. 29.

Fig. 28.—Ultramarine Crucible Furnace. Fig. 29.—Ultramarine Open-hearth Furnace.

upon being heated in a crucible, then becomes a fine blue. After thorough washing and drying the pigment is ready for use.

Smalt is a kind of pulverised glass prepared by fusing cobalt ore with potash and quartz.

Cœruleum is a stannate of cobalt prepared in a somewhat similar manner to Thenard's blue, using a compound of tin in place of alum. The cobalt blues are rich colours, and are very permanent.

Cobalt ultramarine is prepared by mixing 16 parts of freshly precipitated alumina with 2 parts of cobalt phosphate or arsenate, the mixture being dried and slowly heated to redness.

Blue verditer is a pigment of a light-blue colour, and was formerly much used by wall-paper manufacturers. A solution is prepared from sulphate of copper (bluestone) in an earthenware vessel, and another solution is made in a similar manner from carbonate of soda. The soda solution is now added to the copper solution. When a precipitate falls, the clear water is syphoned off, and the mass is treated with more water, which is again syphoned off. The mass is then treated with a weak solution of caustic soda, which is thoroughly mixed into it until the desired colour is obtained. Finally the mass is again washed with water to free it from soda. It is sold ready for use in a pulp, or may be dried and ground into a fine powder. This is but one of several methods.

Another method of making blue verditer is to mix together solutions of calcium chloride and copper sulphate, and precipitate with slaked lime. Bremen green and green verditer have been prepared by modifications of the above methods.

Lime blue, very little used since the introduction of artificial ultramarine, is a hydrated carbonate of copper, with an addition of sulphate of lime. It was prepared by adding ammonium chloride to a solution of copper sulphate, and mixing with slaked lime; after standing for some time the blue precipitate was filtered off, washed, and dried. It was largely used at one time, but it has been almost entirely superseded by artificial ultramarine.

Mountain blue is prepared by grinding azurite—the native hydrated carbonate of copper—it is a most useful pigment, and the most stable of the copper blues, its composition being represented by the formula $2CuCO_3$, CuH_2O_2.

Indigo is an extremely valuable colouring material from the dyer's, but not from the painter's, point of view. It is not suitable for working up with oil, being a bad drier and, moreover, not having any body. It can be used for tinting white-lead paint, but better and cheaper pigments are available for that purpose. It is, however, one of the most extensively employed dyestuffs both of past and present times. It is derived from the indigo plant, *Indigofera tinctoria*.

CHAPTER V.

CHROME PIGMENTS.

THE chromes are an exceedingly fine series of pigments, varying in colour from a pale yellow to a fiery red. They are known by the names of "pale," "medium," "dark," orange, and red chromes.

The true chromate of lead $PbCrO_4$ is a yellow verging upon orange; the pale, medium, and dark chromes all contain sulphate of lead, the amount decreasing as the tint deepens.

The orange and red chromes are basic chromates of lead, the most basic being the reddest, the ordinary red chrome having the composition $PbCrO_4PbO$.

As pigments, all the chromes are excellent; they have good body, cover well, and are fairly permanent in oil under ordinary conditions; but they blacken slowly in oil when exposed to foul gases, and rapidly as water-colours.

The chromes are also blackened by pigments containing sulphur, such as cadmium yellow. Another defect of these colours is that they exert an oxidising action upon organic pigments, gradually bleaching them, the chrome becoming greener in colour owing to reduction.

Lead chromes must not be mixed with ultramarine, lime blue or cadmium yellow, or with any pigment containing sulphur, as the pigment will turn brown, owing to black sulphide of lead being formed. When the lemon and middle shades are mixed with whiting, lime or any alkali, they turn an orange tint, and should not be used for distempers.

Lead chromes are used extensively by the house-painter for a variety of purposes. Mixed with Prussian or Brunswick blue, they form the well-known Brunswick greens. Chromes are prepared in a variety of shades, from primrose to red, known commercially by the following names: Lemon chrome, middle chrome, orange chrome, Derby red, and mock vermilion or vermilionette, the preparation of this

being described in the chapter on red pigments (see pp. 95 to 102).

The base of all lead chromes is chromate of lead ($PbCrO_4$), a compound of the basic oxide of lead and the acid oxide of chromium, and is prepared by adding and stirring together a bichromate of potash solution and a solution of acetate or nitrate of lead, the resulting precipitate being chromate of lead.

Before giving proportions of the ingredients used in preparing chromes, it will be instructive to describe the appliances used in preparing by precipitation such pigments as chrome yellows, Prussian, Chinese, and deep blues, greens, vermilionettes, madder red, etc. They are of very simple character, usually consisting of several large wooden tubs or becks, the sizes varying according to the quantity of colour required. Fig. 30 shows how the vats are arranged at most colour works. The precipitating or mixing tubs or becks A are made of 1½-in. deal, and each hold about 400 gal. Smaller tubs B are used for dissolving the various ingredients. Plug holes for running off at different times during the precipitating are indicated at C; branch steam pipes to the various tubs for dissolving at D; while E indicates a copper-bound indiarubber water pipe, 1½ in. in diameter. The tubs B are usually lined with sheet-lead to resist the action of the acids, and are sometimes placed on the floor above, with pipes running through to the precipitating tank. This method is adopted in order to prevent the poisonous vapours from contaminating the air breathed by the workmen.

The method generally adopted in preparing pigments by precipitation is as follows: When a green pigment is to be prepared, it requires the whole of the plant described in Fig. 30. A bichromate of potash solution is prepared in a vat such as that shown at B, and another solution of lead acetate or nitrate in one of the vessels A. The solution in B is now run steadily while continually stirring into A. It is then allowed to repose, and the clear water run off through plugs C. The vessel is then filled with water, and the contents are well stirred, the water being finally run off as before, when a precipitate of chrome will be formed in one of the vessels A ready for further treatment.

In vats B a solution made from fresh ferrous sulphate

(copperas) in one vat, in the other a solution of equal strength of yellow prussiate of potash, is boiled by means of a steam jet. The ferrous sulphate is now added to the potash solution, and both are boiled together for some time (acids being added in some formulæ at this stage of the process). It is then run into the empty large vat A, which has been half-filled with cold water; and the deep Prussian blue thus made, after being well stirred, is allowed to precipitate, and the water run off. Cold water having been again poured in, the mass is stirred and precipitated as before, this being essential to free it from acids, etc. Some colours require washing three times. The contents of one vat are now ladled into the chrome yellow in the

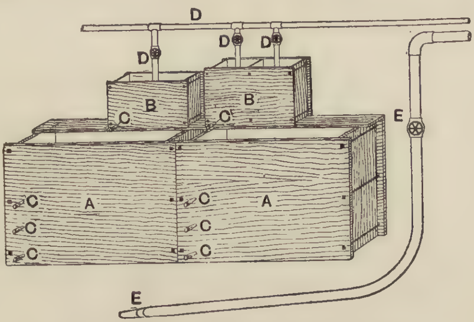


Fig. 30.—Pigment Preparing Plant.

other; this produces a pure Brunswick green. The chrome is continually stirred whilst adding the blue. The contents of the vat are allowed to precipitate, the water is run off, and the pigment is placed upon filters, then pressed and dried ready for use. When cheaper grades of colour are required, the solutions are run into the vats, to which have been added barytes, mineral white, whiting, etc.

The appliances used for the preparation of lead chromes are identical with those just described, and illustrated by Fig. 30. The lead acetate or nitrate is dissolved in one vat with a certain volume of water. In another vat a specified quantity of bichromate of potash or soda is dissolved, and in some instances Glauber's salts are added, and both are dissolved together. When the contents of

the first vat are dissolved, which may be facilitated by steam if necessary, the contents of both vats are run together into the precipitating vat, where they are continually agitated by means of large wooden stirrers and afterwards allowed to repose a short time in order to precipitate. The water is then run off through plugs, and the vat is filled up with cold water and well stirred to free it from any impurities, acid, etc. In some cases three washings may be found necessary. After the washing has been successfully accomplished, the water is run off as before and the colour taken out and placed on linen strainers or filters to drain, and after being dried in the stoves it is ready for grinding into paint.

The following table shows the proportions of ingredients used in making pure chromes:—

	Lemon.	*Middle.*	*Deep.*	*Orange.*
Lead acetate or nitrate ..	26	26	26	26
Bichromate of potash or soda	6	7	8	8
Sodium sulphate	8	5	—	—
Caustic soda	—	—	—	2

By varying the proportions of the bichromate and sodium sulphate, almost any shade of chrome may be obtained. Either the acetate or the nitrate of lead, and either the bichromate of potash or the bichromate of soda, may be used.

The cheaper qualities of lead chromes, which are not chemically pure, are reduced by adding during the precipitating process barytes, gypsum, and china clay.

For preparing on a small scale the lead chromes and other pigments produced by precipitation, three wooden tubs (Fig. 31) may be used, two of the tubs, A, B, being supported upon a trestle, the other, C, resting upon the floor. Steam pipes D are provided for blowing steam through the liquids. When the production is undertaken upon a large scale, large barrels or tanks are used instead of tubs for preparing the solutions, and a tank is employed

for the precipitation. As a preliminary in preparing a pure chrome colour, the two tubs A and B are partly filled with water; a weighed amount of bichromate of potash is placed in one tub, and an equivalent amount of acetate of lead in the other. Steam is now turned into both tubs until the salts are dissolved, when it is shut off, and the liquids are allowed to cool. The solutions being quite cold, they are either ladled into the tub C or emptied simultaneously by taps, agitation being produced by stirring with a stick. The chrome colour quickly settles

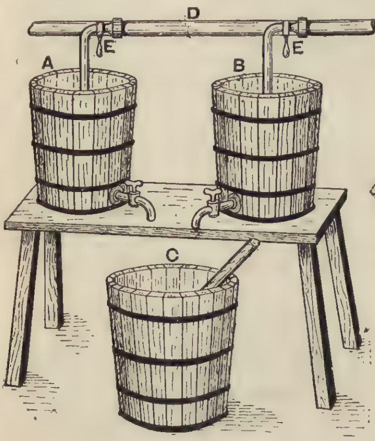


Fig. 31.

Fig. 31.—Precipitating Plant

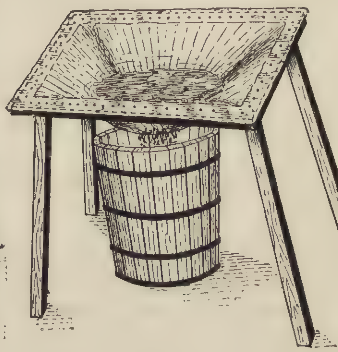


Fig. 32.

Fig. 32.—Cloth Filter.

out, leaving the supernatant (or floating) liquid clear. The clear liquid is syphoned off and fresh water added, the pigment stirred up and allowed to settle—this treatment being several times repeated for the purpose of removing all the soluble salts; the moist pigment is then collected by filtration.

When small quantities only are being manufactured, a simple filter like that shown in Fig. 32 is very useful. The filter consists of a piece of linen cloth fixed to a square frame of wood by copper tacks, and the whole supported by four wooden legs. When the moist pigment is placed

upon the linen cloth, the water rapidly drains off; the cloth may then be pressed gently with the hand, and hung up in a warm place for the pigment to dry.

When large quantities have to be dealt with, the pigment is collected by pouring it into filter bags, which are then pressed in a wood press; or the liquid containing the pigment in suspension is run through a filter press (Fig. 33), which allows the material to be filtered, washed, and pressed in a very short space of time. The pigment still contains some water, so that it requires to be dried. It is broken up into small lumps, which are placed in open pots or dishes, and these are arranged side by side on shelves in a drying chamber kept at a moderate temperature by a coil of steam pipes.

The equation showing the formation of the chromate of lead is as follows:—

$$\underset{\text{Lead acetate.}}{2Pb(C_2H_3O_2)_2 3H_2O} + \underset{\text{Potassium bichromate.}}{K_2Cr_2O_7} = \underset{\text{Lead chromate.}}{2PbCrO_4} +$$

$$\underset{\text{Potassium acetate.}}{2KC_2H_3O_2} + \underset{\text{Acetic acid.}}{2HC_2H_3O_2} + \underset{\text{Water.}}{5H_2O.}$$

The amounts of the precipitating agents to be used are calculated as follows:—

The atomic weights of the different elements contained in each compound are added together, and the sum is known as the molecular weight of the compound. Taking lead acetate as an example, this substance contains:—

		Units.
1 atom of lead weighing		207
4 atoms of carbon ,, ...	$12 \times 4 =$	48
6 ,, hydrogen ,, ...	$1 \times 6 =$	6
4 ,, oxygen ,, ...	$16 \times 4 =$	64
Also in the water of crystallisation contained in the salt—		
3 atoms of oxygen weighing	$16 \times 3 =$	48
6 ,, hydrogen ,, ...	$1 \times 6 =$	6
Weight of 1 molecule of lead acetate ($Pb(C_2H_3O_2)_2 3H_2O$)		379

One molecule of potassium bichromate contains—

2 atoms of potassium weighing ..	$39 \times 2 =$	78
2 ,, chromium ,, ..	$52\frac{1}{2} \times 2 =$	105
7 ,, oxygen ,, ..	$16 \times 7 =$	112
Weight of 1 molecule of potassium bichromate ($K_2Cr_2O_7$)		295

As shown by the equation given above, two molecules of lead acetate or 758 parts are required for one molecule of bichromate or 295 parts; the same proportions hold good for ounces, pounds, or hundredweights.

In the old rule-of-thumb days the materials were rather indiscriminately added; but now the prices are cut so fine that waste must as far as possible be avoided. Therefore, proportionate quantities are always calculated beforehand. If the above proportions be used, there will be no excess of either reagent, and the amount of pigment yielded can also be calculated, though allowance has to be made for unavoidable loss in collection and drying. The above quantities will yield two molecules of lead chromate

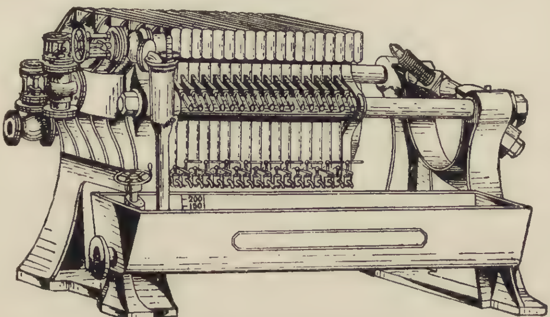


Fig. 33.—Filter Press for Pigments.

weighing 647 units as shown below. One molecule of lead chromate contains:—

			Units.
1 atom of lead weighing		.. ..	207
1 ,, chromium	,,	.. ..	$52\frac{1}{2}$
4 atoms of oxygen	,,	$16 \times 4 =$	64
Weight of 1 molecule of lead chromate ($PbCrO_4$.)		.. ..	$323\frac{1}{2} \times 2 = 647$

This example has been given rather fully because it will serve as an illustration of the method used in all cases where pigments are prepared by precipitation. In practice, part of the bichromate is almost always replaced by a calculated equivalent of sulphuric acid or sodium

sulphate, producing a pigment containing, besides chromate of lead, a variable quantity of sulphate of lead. By varying the proportions of bichromate and sulphuric acid it is possible to obtain almost any tint of yellow, the hue of these pigments being purer than that of the normal chromate of lead. This is a great advantage, because it lowers the cost of production, and, at the same time, the products formed will give better results when mixed with other pigments. It is absolutely essential for the production of good chrome yellows that the solutions shall be used cold, and the pigments filtered off rapidly. Other salts of lead, such as the nitrate, are sometimes used in place of the acetate.

Orange chromes are prepared in a variety of ways, but chiefly by the action of caustic soda upon chrome yellow, or by boiling white-lead with chromate. In the first method the yellow chrome is simply warmed with a dilute solution of caustic soda. A portion of the chromate is then decomposed and replaced by oxide. It is possible to obtain tints ranging from pale orange to brilliant scarlet by varying the strength of the soda solution.

$$\underset{\text{Lead chromate.}}{2PbCrO_4} + \underset{\text{Caustic soda.}}{2NaHO} = \underset{\text{Basic chromate.}}{PbCrO_4PbO} + \underset{\text{Sodium chromate.}}{Na_2CrO_4} + \underset{\text{Water.}}{H_2O}$$

A portion of the chromic acid is here wasted, but if the chrome yellow contains sulphate of lead, this is prevented, as shown in the following equation:

$$\underset{\text{Lead chromate sulphate.}}{PbCrO_4PbSO_4} + \underset{\text{Caustic soda.}}{2NaHO} = \underset{\text{Basic chromate.}}{PbCrO_4PbO} + \underset{\text{Sodium sulphate.}}{Na_2SO_4} + \underset{\text{Water.}}{H_2O}$$

In the second method the basic chromate of lead is formed by boiling white-lead with bichromate previously neutralised with caustic soda or potash, so as to form chromate:—

$$\underset{\text{White lead.}}{2[2PbCO_3.PbH_2O_2]} + \underset{\text{Potassium chromate.}}{3K_2CrO_4} = \underset{\text{Basic chromate}}{3[PbCrO_4PbO]} + \underset{\text{Potassium carbonate.}}{3K_2CO_3} + \underset{\text{Carbonic acid.}}{CO_2} + \underset{\text{Water.}}{2H_2O}$$

The usual commercial method of preparing orange chrome is to make a quantity of lead chrome, add the

alkali (lime or caustic soda) and boil by means of steam until the required shade is obtained. By adding variable proportions (from 8 lb. to 15 lb.) of caustic soda, various shades of orange chrome, Derby red, Chinese red, American vermilion, and chrome red may be obtained.

The majority of commercial samples of orange chrome contain a varying proportion of lead sulphate, introduced by precipitating the lead solution by a mixture of a sulphate such as Glauber's salts and the bichromate. These impure colours are only slightly inferior in brilliancy to the pure ones, but their staining power depends on the amount of chromate they contain.

The lead chromes may easily be tested for purity by boiling a small quantity of the suspected sample in strong hydrochloric acid until it is entirely decomposed. Should there be an insoluble residue, this will consist of china clay, barytes, or gypsum.

Chrome red, a pigment also known commercially as Derby red, mock vermilion, and Persian red, is a basic chromate of lead made in a variety of shades from pale orange to deep scarlet red.

Chrome reds may be modified somewhat by altering the proportions of the bichromate and alkali and the time of boiling. The larger the quantity of alkali added the deeper the resulting red, as may be observed by the following table:—

Ingredients.	*Orange.*	*Scarlet.*	*Deep.*
Lead acetate or nitrate	11	11	20
Bichromate of potash or soda	4	4	10
Caustic soda or sodium hydrate ..	1	$1\frac{1}{2}$	3

The essential feature in the preparation of chrome reds is the finish or washing of the colour after boiling; all traces of alkaline matter should be carefully removed by washing, otherwise the durability of the pigment will be affected. Chrome reds are good bodied pigments of exceptional covering power and brilliancy, and are durable under ordinary circumstances. But when submitted to

sulphurous gases they turn black owing to black sulphide of lead being formed. They should not be compounded with pigments containing sulphur, such as ultramarine, oxides, and cadmium yellow, which have an effect similar to that of sulphurous gases.

For testing lead chromes, place a small quantity of the pigment in a test tube, add about three times its volume of strong sulphuric acid, and heat until completely decomposed; then allow it to cool, add an equal volume of water and a little alcohol, filter, and wash well. The residue, if the pigment is pure, will be lead sulphate $PbSO_4$; but it will contain barytes, china clay, or terra-cotta if the material is adulterated. Boil the residue with strong hydrochloric acid, and then filter it whilst hot; the residue will be the adulterant.

Besides the lead chromes there are a few chromates containing other metals than lead that are used as pigments; the chromates of zinc and barium are the chief of these.

Zinc chromes may be prepared by mixing together solutions of zinc sulphate and potassium chromate, but the precipitation is only partial, and there results a large loss of material in solution. By adding the chromic acid or bichromate of potash in variable proportions, any shade of zinc chrome may be prepared.

Another and a more satisfactory method is to boil zinc oxide (zinc white) with a solution of potassium bichromate; the zinc oxide is thereby partly converted into chromate. The pigments formed by the above-described methods are all basic chromates of zinc; they have a fine yellow colour and good covering power, but yield a smaller variety of tints than the lead chromes.

Pure zinc chrome may easily be tested for purity by treating it with acetic acid, which renders it completely soluble. Any residue indicates adulteration with barytes, china clay, whiting, etc. Again, the purity of a sample of zinc chrome may be determined by treatment with hydrochloric acid. A small quantity of the pigment should be warmed with the dilute acid, and there should be no effervescence due to the presence of carbonates (chalk, white-lead), and there should be no insoluble residue (barytes, gypsum, kaolin). As the solution cools, it should

remain quite clear; a deposit of crystals on cooling indicates lead (lead chrome or white-lead). On passing sulphuretted hydrogen through the above solution there will be a white precipitate of sulphur, but no blackening (lead compounds). Zinc chrome should yield a colourless solution when boiled with water; a yellow-coloured liquid would indicate soluble chromates (chromates of lime or strontium).

The chief advantage of zinc chrome as a pigment is that it is almost permanent, practically unaltered by light and moisture, and, unlike the lead chromes, it is unaltered by sulphuretted hydrogen; being a pure pale yellow, it is useful for forming greens and other mixed tints. It is used in the preparation of washable distempers, enamels, etc. The defects of zinc chrome are paleness of tint, because it contains much zinc oxide; it therefore will not stand dilution.

Lemon chrome, a pigment but little used, is the chromate of barium, and is prepared by precipitating a solution of barium chloride with potassium chromate. The name lemon chrome is often used for a pale lead chrome.

Chrome green is a very fine pigment much used by artists and house painters for high-class decorations on account of its permanence whether mixed in oil or in water. It possesses excellent covering power, and may be compounded with other pigments without interfering with their chemical properties or durability. Chrome green is frequently adulterated with the lead chromes and the Brunswick greens. The adulteration may be detected by boiling a sample with dilute hydrochloric acid, when the development of a yellow appearance would indicate the presence of chrome yellow. Chrome greens are used extensively for printing wall-papers and calico, and for this purpose the pigment is usually sold under the name of Guignet's green, in a pulp form, containing from 25 to 40 per cent. of moisture.

Originally the name chrome green was applied to those pigments which owed their colour to chromic oxide; now, however, many of these greens are simply mixtures not containing any chromic oxide.

Chrome green varies in composition, but usually consists of oxide of chromium Cr_2O_3. There are several methods of preparing these greens. The following has been found

to give highly satisfactory results:—A mixture made of 16 parts of bichromate of potash and 7 parts of boracic acid is ground or levigated with water under flat stones (see Fig. 24, p. 53) into a stiff paste, after which it is plastered in layers in a reverberatory furnace, and calcined for from two to five hours at a moderate heat. It is then taken out of the furnaces and agitated in large vats of water to remove the acids, after which it is ground under an edge runner (see Fig. 25, p. 55), levigated again, washed and filtered, and placed in suitable stoves to dry. The product is said to be a hydrated oxide of chromium, and is the pigment known as Guignet's green or viridian.

Chrome green, when properly prepared, is not affected by acids or alkalies, and in this respect it differs from all other greens.

There are many other methods of preparing chrome greens, chief among which are:—

1. By heating ammonium chromate;

$$2(NH_4)_2CrO4 = 4NH_3 + H_2O + Cr_2O_3.$$

2. By heating mercuric chromate in a retort, mercury distilling over;

$$2HgCrO_4 = 2Hg + Cr_2O_3 + O_5.$$

3. By heating bichromate of potash with reducing agents, such as sugar, starch, etc.

The chrome greens produced by the above methods are perfectly permanent under all conditions; those produced by means of mercuric chromate or boracic acid are the best greens, the others being more inclined to be greyish or yellowish.

In making Guignet's green by the method explained above, if phosphate of soda be used in place of boracic acid a yellowish-green pigment containing chromium and phosphoric acid is produced.

There are now sold under the name of chrome greens certain pigments containing Prussian blue and chromate of lead, with more or less barytes or gypsum. These are noticed under the head of Brunswick green (see p. 88).

CHAPTER VI.

LAKE PIGMENTS.

THE lakes are defined as pigments formed by absorbing colouring matter—animal, vegetable, or coal-tar—from an aqueous solution by means of metallic bases.

The madder lakes vary in colour according to the method of preparation, and are known as madder carmines and reds, also as rose, purple, and brown madders, etc. As pigments, they have good covering power, and they are uninfluenced by exposure to air or foul gases. On exposure to sunlight, madder lakes fade slightly, but they are much less affected than the cochineal lakes, or, in fact, any other lake colours.

It may be mentioned that the madder lakes are weak compounds of the colouring matters of madder with hydrate of alumina ($Al_2(HO)_6$), but no definite formula can be applied to them at present. They are expensive pigments, and therefore liable to be adulterated with the cheaper lakes and mineral matters. They are prepared from the roots of the madder plant, there being several species of the genus *Rubia* which yield, by proper treatment, brilliant red lakes. Among these the European madder *Rubia tinctorum*, and the Indian species, *Rubia cordifolia* and *Rubia sikkimensis*, may be particularly noted. The European madder plant (*Rubia tinctorum*), is cultivated extensively in the Levant, Greece, Italy, the south of France, Alsace, Silesia, and Holland. Avignon, the capital of the department of Vaucluse, in the south-east of France, is a most important centre of cultivation, yielding about one-half of the entire quantity consumed.

In the preparation of madder lake, the plant roots, from 1 ft. to 2 ft. in length, and about $\frac{1}{4}$ in. in thickness when fresh, are dried by artificial heat, freed from their shrivelled skin, and roughly pounded to a powder, in which form they are sent to market. The powder is then

treated with a dilute solution of sulphuric acid, and boiled with a solution of alum to extract the colouring matter, to which a solution of carbonate of soda is added. The lake colour is collected upon a filter cloth and washed with distilled water until all the soluble salts are removed; the moist pigment is then moulded into small drops and dried.

Several other processes for the preparation of madder lakes are known. In some the root is steeped for several hours in water, when a peculiar fermentation takes place, and the colour is liberated without the previous treatment with sulphuric acid; in others, "garancine," a preparation of madder containing the colouring matter, is used in place of the madder root.

The colouring matters of madder do not exist ready formed in the roots; the substances from which they are formed are called "glucosides," because they may be split up into glucose—a kind of sugar—and several colouring matters named alizarin ($C_{14}H_8O_4$), purpurin ($C_{14}H_8O_5$), etc. Alizarin and purpurin are the chief colouring matters of the plant, but the alizarin plays the most important part in the formation of the lakes. The preliminary treatment with dilute acid, and the fermentation, also mentioned, serve to decompose the glucosides present in the roots, and thus set the colouring matters free.

Since the discovery of a method for preparing both alizarin and purpurin from anthracene ($C_{14}H_{10}$), a coal-tar product, the natural product has been largely superseded by the artificial colouring matters both for dyeing and for pigment making. Lakes are formed from the artificial alizarin and purpurin by solution in alkali, and precipitation with the hydrate or a salt of alumina.

With regard to the lake known as alizarin lake, it has already been noted that alizarin is now obtained from coal tar, this yielding a very fine red lake, valuable for its permanency when precipitated with aluminium salts. The brightness of the shade obtained depends very largely on the purity of the chemicals used, as the slightest trace of iron will darken the colour. An earthenware vessel has to be used for this reason, and as the solutions must all be very dilute, only small batches can be made. Alizarin being insoluble in water, but readily soluble in alkaline solutions, the solutions are made as follows: The alizarin

is dissolved in a dilute solution of soda carbonate and soda phosphate, and to this is added some alizarin oil, in weight about 5 per cent. of that of the alizarin used. In another vessel the aluminium sulphate or ammonia alum used is dissolved, and added very slowly to the other solution, as carbonic acid is freely evolved. Finally a small quantity of calcium acetate is added. The lake, however, is not precipitated at once, but after standing for some time heat is applied, and the whole is slowly raised to the boil and boiled for one to two hours till the colour is developed, when it is washed and dried as usual.

The reaction in this precipitation is somewhat obscure, but it has been found that both the phosphate and the calcium acetate are required for the production of bright shades. The results by this method are good, but rather dark, and brighter reds are obtained when the colour is developed by low steam pressure in a closed vessel.

Eosin lakes are known as "vermilionettes" and "royal reds." They are easy to produce, the eosin being precipitated by means of lead acetate, and occasionally aluminium sulphate, on a base of either orange lead or barytes, or a mixture of these. The base is mixed with water, and kept suspended as usual, when the eosin in solution is added, and precipitated by the solution of lead acetate. The colour is washed and then filtered, dried, and ground. The best qualities are struck on orange lead. The amount of eosin used varies with the price of the colour, from 1 lb. to 2 lb. per cent. of base and upwards, and with it, of course, the amount of precipitant required.

Chemically, eosin is tetrabromfluoresceïn ($C_{20}H_8Br_4O_5$), this being a coal-tar derivative in the form of red or yellowish-red crystals. It forms a potassium salt, a red powder, and this is the commercial eosin.

In testing alizarin lake, an effort is made to estimate the percentage of alizarin it contains. It must be remembered that this pigment consists of alizarin combined with or precipitated upon a base of alumina; when this lake is boiled with dilute hydrochloric acid, the alumina is dissolved out, leaving the alizarin as an insoluble powder; this method allows of the separation and estimation of the colouring principle. Ten to 15 gr. of the sample are weighed out and boiled for about half an hour with

dilute hydrochloric acid, the liquid is allowed to cool, and then filtered through a filter paper which has been previously dried at 100° C. and weighed. The alizarin is washed on to the filter paper with cold distilled water, and the washing is continued until the filtrate is quite free from acid; then the filter paper and its contents are dried and weighed, the drying being continued till the weight is constant. The difference between the weight of the filter paper alone and with its contents represents the amount of alizarin in the quantity taken, from which the percentage may be calculated.

A modification of this method which will give more accurate results is: after decomposing the lake with acid, to place the liquid in a separating funnel, add ether, and shake; run off the aqueous liquid, then collect the ethereal solution of the dye in a weighed flask, evaporate off the ether, and dry the alizarin.

The spirit test for alizarin and madder lake detects any adulteration. A pure lake yields no colour when digested with alcohol, whereas most of the other lakes, and especially the pigments containing other coal-tar colours, yield some of their colouring matter to the spirit.

The bases used in preparing lakes or pigments from the coal-tar colouring matters are barytes, gypsum, whiting, china clay, and zinc white. The precipitating agents are tannic acid, tartar emetic, sulphate of alumina, lead acetate, barium chloride, aluminium acetate, and sulphate of iron; alkalies, such as ammonia or carbonate of soda, are also used as assistants when required for rendering solutions neutral or slightly alkaline.

Yellow lakes are organic pigments produced by the precipitation of vegetable dyes upon a base of alumina. The yellow dyes used are obtained largely from the bark of certain American black oaks (*Quercus tinctoria*, the dyer's oak). The juice of the berries from buckthorn trees, known in commerce as Persian or Turkish berries, is also used. The infusions of quercitron bark or buckthorn berries are made with hot water; alum and pearlash or carbonate of soda added to this infusion cause a precipitate of alumina, $Al_2(HO)_6$, which carries down most of the colouring matter; the yellow lake is filtered off and dried. Yellow lakes are transparent pigments, and they fade rapidly in

sunlight; their chief uses are for paper staining and distemper painting.

Dutch pink is a wood lake prepared by making a decoction of quercitron bark or fustic, staining, neutralising the liquor with chalk ($CaCO_3$), and then running it into the tub containing the base, terra alba, which is suspended in water, and finally precipitating the colouring matter on the base by means of lead acetate or aluminium sulphate. The colour thus made is washed and dried after standing some time.

Carmine, crimson lake, etc., are the brilliant pigments formed from the cochineal insect, *Coccus cacti*, which lives on some species of cacti, *Opuntia Tuna*, *Nopalea cochinillifera*, etc. The cochineal insect was introduced into Europe in 1523 from Mexico; it is of small size, and of a deep red or mulberry colour. The insects are scraped from the cacti, willed in boiling water, and dried in the sun. About 70,000 go to the pound weight of cochineal. The cochineal insect appears in commerce as small, round, flattened, and somewhat wrinkled grains of a dark red colour.

Carmine is prepared from these insects by infusing them in boiling water, and, a small quantity of alum or other substances having been added, the liquid is allowed to stand for several days. The carmine is gradually precipitated; it is collected, washed, and dried in the usual manner. The filtered liquid is always coloured by some of the carmine remaining in solution, and from it scarlet lakes are prepared, either by suspending in it some moist hydrate of alumina, which absorbs the colouring matter, or by adding a solution of alum and then carbonate of potash, the same result being obtained.

Carmine appears to be a lake consisting of a large quantity of the colouring matter combined with only a small proportion of alumina, and it is the most brilliant of these pigments; the crimson lakes, containing more mineral matter, are not so powerful.

In the manufacture of commercial carmine the process given above is not usually followed. Instead, it is as follows: To produce a carmine of a deep scarlet tint, boil in a copper vessel with 21 gal. of pure spring water for seventeen minutes, $3\frac{1}{4}$ lb. of powdered cochineal and $1\frac{1}{2}$ oz.

of carbonate of potash; remove the vessel from the fire, cool down to 100°, and add 3 oz. of powdered alum and 1 dr. of cream of tartar. Agitate the mixture for several minutes with a bone spatula, and allow to settle for twenty minutes; the clear liquor is then taken off by means of a syphon and placed in a perfectly clean copper vessel. Now add 1½ oz. of pure isinglass dissolved in ½ gal. of water; again place the mixture on the fire, and agitate with the bone spatula for ten minutes; then take it off and allow to stand for two or three days, when the carmine will all be settled. It is then collected and dried previous to being ground into paint. Success depends on the quality of the materials used: they should be the finest that can be procured.

Carmine generally put up in collapsible tubes is not absolutely pure; it usually contains several adulterants, such as vermilion, Derby red, orange chrome, and the aniline lakes and chrome reds. The following is a recipe of one of the principal manufacturers: carmine 3 lb., deep orange chrome ½ lb., vermilion ½ lb., terra alba 7 lb., refined poppy oil, 3 pt.

Pure carmine is exceedingly light, and is not a permanent pigment; it is soluble in ammonia—a test by which its purity is determined, as the insoluble impurities are left. The cochineal pigments are splendid crimson reds, but they fade very rapidly in sunlight.

In testing crimson lake, a pure crimson lake should dissolve entirely in a solution of caustic soda, yielding a bluish-carmine solution; it will precipitate out again by carefully neutralising with dilute acid. As a rule, pure crimson lake does not yield colour to alcohol, whereas the aniline so-called lake colours usually tint alcohol very strongly because the colours are but weakly held by the base. The colour of cochineal lake becomes bluer with ammonia and yellower with an acid, but the behaviour of lakes containing aniline colours will vary with the nature of the colour used. Crimson lake, when carefully heated in a porcelain dish, should burn away, leaving a small quantity of a light white ash; a large amount of residue, either white or coloured, shows evidence of adulteration with mineral matter.

Crimson lake, being a bad drying pigment, should be

ground with boiled oil, if oil is used; but it would be better to apply the lake ground in turps and to varnish over it, or to grind it in a quick-drying varnish. In any case it is a fugitive colour, fading in bright sunlight very rapidly.

Several other red lakes are made from natural products, such as Brazil wood, etc.

Indian lake is prepared from "lac dye" produced by treating stick lac with very dilute alkali. As the stick lac is an exudation produced by a species of Coccus (*C. lacca*), the colouring matter resembles that of carmine and the cochineal lakes. Particulars of the method of obtaining the stick lac—one of the many varieties of lac—are given in the chapter on varnishes and varnish making at the end of this book. It may be said here, however, that gum lac, in its crude form, is gathered from the twigs of trees, where it is left after the puncture of the bark by the insects known as *Coccus lacca*. This is generally accepted by the commercial world as gum lac or stick lac, the products after various stages of manufacture being known as seed lac, shellac, lump lac, and cake lac, further classes or grades being lemon, orange, garnet, or button lac. When the gum is separated from the twigs, the first object is to free the resinous product from the colouring matter; this is done by frequent washings, the residue being afterwards evaporated to form cakes of dye known as lac dye, from which Indian lake is prepared.

CHAPTER VII.

GREEN PIGMENTS.

THE green pigments used so extensively by the house painter are manufactured in a great variety of shades, those chiefly used being the Brunswick, emerald, chrome, zinc, mineral, sap, and Victoria greens.

Brunswick green, known also as Bremen green, and already referred to several times in Chapter V., is the most important of the above group. It may be combined or mixed, without being chemically affected, with nearly all other pigments, the exceptions being those containing sulphur or an alkali, as ultramarine, lime blue, whiting, or lime. Brunswick greens are fairly permanent in ordinary circumstances, but darken somewhat under the influence of sulphurous gases, the sulphur attacking the lead chromate used in the preparation of the green; whilst the alkali in the lime and whiting would turn it a reddish brown colour, so that Brunswick green cannot be used in distempers and washes.

Brunswick greens are now prepared by two processes. One method is to mix chrome yellow with Prussian or Brunswick blue under an edge-runner mill until the colours are thoroughly incorporated, when they are taken from the mill and passed through very fine sieves (about forty-eight meshes to the inch), to prevent streakiness and to produce a more uniform colour. By mixing the blues and chromes in variable proportions, any shade of green may be produced. When the reduced or cheaper qualities are required, barytes, Paris white, and gypsum are added, and all the ingredients are ground together as before.

The other process, which is known as the wet method, consists in preparing the greens direct from the raw materials, green copperas, acetate of lead, yellow prus-

siate of potash, bichromate of potash, and barytes. The following table gives the quantity of each material used in order to obtain the three shades, pale, middle, and deep:—

	Pale.	*Middle.*	*Deep.*
Bichromate of potash	4	9	10
Yellow prussiate of potash	1	3	4
Acetate of lead	12	27	28
Ferrous sulphate	1	3	4
Barytes	100	100	100

The method adopted for mixing the raw materials in making Brunswick greens by the wet process is fully described on pp. 70 and 71, an illustration of the necessary appliances being given by Fig. 30, p. 71.

For testing Brunswick greens, boil a small quantity of the green with strong hydrochloric acid for about eight minutes, then filter whilst hot, and wash well with boiling water. The residue consists of barytes and Prussian blue. It is next subjected to a considerable heat until the blue is entirely decomposed. It is then treated with a mixture of hydrochloric and nitric acids and boiled well, which will remove the oxide of iron. It is then well washed, filtered, and weighed, the residue being barytes.

Scheele's green was discovered in the year 1778 by Scheele, a Swedish chemist, well known by reason of his association with the discovery of oxygen. To prepare this colour, 1 part of powdered white arsenic (As_2O_3) is boiled with 2 parts of pearlash (K_2CO_3), and 35 parts of water; after solution is complete it is poured into a solution of copper sulphate, the resulting green pigment being washed and dried. This pigment is a basic arsenite of copper, containing about 50 per cent. copper oxide, 42 per cent. arsenic trioxide, and 8 per cent. of water; its composition may be represented by the formula $CuAsO_3CuH_2O_2$ Scheele's green is of a dull yellowish-green colour, with very little covering power. It has nothing to recommend it, and being extremely poisonous, should be avoided.

Emerald or Schweinfurt green, a finer arsenical green than Scheele's, has been more largely used. It may be

prepared by boiling white arsenic with carbonate of soda, then pouring the solution into copper sulphate, as above, partially dissolving the Scheele's green thus produced with a small quantity of acetic acid, and allowing it to stand; the pigment separates out as a brilliant green crystalline mass.

Emerald green is a fine pale bluish-green pigment, and is considered to be one of the brightest pigments produced. Substitutes made from the coal-tar dyes are of a more or less fugitive character, and lack the brilliancy of tint that characterises emerald green, which, used alone, is a fairly permanent pigment. If, however, it is mixed with pigments that are chemically antagonistic to it, its brilliancy may easily be destroyed. Such pigments as ultramarine, cadmium yellow, or any pigment containing sulphur, will destroy emerald green, after a short exposure, by turning it black, owing to the formation of black sulphide of copper. Distempers, whiting, lime, and any colour containing alkaline bodies, destroy emerald green.

This pigment is very poisonous, being, as already shown, a compound of copper, arsenic, and acetic acid. It is therefore generally avoided for interior decoration. In America it is much used in the agricultural districts (where it is known as Paris green) for killing insects.

A common Continental method of preparing emerald green is as follows: A solution of copper sulphate is made by dissolving 100 lb. of copper sulphate in a large volume of water contained in an earthenware or a wooden vessel. In another vessel, 100 lb. of white arsenic is formed into a uniform paste with 3 gal. of water. To the copper solution is added 40 lb. of lime, dissolved in 38 gal. of vinegar, and well stirred. The contents (the arsenic and the copper sulphate) of the two vessels are then mixed and thoroughly agitated with wooden stirrers, after which the mixture is allowed a period of repose, when the green will gradually develop.

Another method of manufacturing this green is to dissolve by heat 10 lb. of verdigris in twice its volume of acetic acid. (Verdigris is obtained by exposing copper plates to the atmosphere in contact with acetic acid; it is a crystalline salt, a basic acetate of copper; see p. 92.) A second solution having been prepared by dissolving

10 lb. of arsenious acid in water, the two solutions are well stirred together and allowed to rest, when a yellowish-green precipitate will fall. The mixture is now heated by means of a steam jet, a few drops of acetic acid being occasionally added in order to convert all the arsenite into aceto-arsenite. The pigment will now gradually develop its characteristic greenish-blue colour. Afterwards it is filtered, washed, and dried at a very low temperature. Much depends on the volume of water used in the preparation, the weaker the solutions, proportionately, the finer the resulting shade of green. The following table, from a German source, gives the analysis of two samples of emerald green:—

Oxide of copper CuO	32·89	32·83
Arsenious oxide As_2O_3	57·40	57·82
Acetic anhydride	6·34	6·56
Sulphur trioxide SO_3	1·60	1·80
Water H_2O	0·85	0·55
	99·98	99·56

A simple test for determining the purity of emerald green is to place a small quantity of the suspected sample in a test tube or ordinary glass vessel, and pour over it about three times its volume of concentrated hydrochloric acid. With a little agitation, it should completely dissolve into a yellowish-green solution. Any residue will be the adulterant—probably barytes, china clay, or gypsum.

A further test is to add a small quantity of ammonium carbonate, which produces a deep blue transparent solution. Any precipitate thrown down will be the adulterant.

Mineral green is used extensively for the manufacture of anti-fouling compositions for ships' bottoms, and it is employed in the preparation of green enamel for Venetian blinds, and for many other purposes where this peculiar shade of green is desirable. Mineral green is a fairly permanent pigment both in water and in oil. It may be obtained both as a natural product and as an artificial manufacture. It is deficient in body and covering power, and has a tendency to fade when placed in too much sunlight. The fumes of sulphur cause it to turn black,

converting it into black sulphide of copper. Mineral greens should not be mixed with pigments containing sulphur, as ultramarine and cadmium yellow. When painted over heated surfaces they turn black, and should therefore be used with caution.

Mineral green of the artificial and more usual kind is prepared as follows: Boil together 18 oz. of white arsenic and 14 lb. of soda crystals until the arsenic is entirely dissolved. In another vessel dissolve 10 lb. copper sulphate in water, and add to it 4 lb. slaked lime. Now add the sulphate and lime solution to the arsenic and soda solution: then stir in 4 dr. of tartaric acid, heat until a temperature of 155° F. is reached, and allow the mixture to remain at this temperature until the colour is fully developed, when the water is run off and the pigment washed, filtered, and dried at a very low temperature.

Verdigris, a pigment which was used in the time of the Romans, is prepared now by a method very similar to that by which it was first produced. At Montpellier and other places in France the skins from grapes used in the wine industry, known as the *marcs*, are placed in casks and allowed to ferment. The fermented marcs are then placed in thin layers alternately with copper sheets in large vats, in which a reaction takes place between the acetic acid formed in the marcs and the copper, with the formation of a basic acetate, or, more properly speaking, several basic acetates of copper; this is verdigris. The plates are removed and dried, the green coating is scraped off, and the plates are again put through the operation. The verdigris is simply washed with water and then dried.

The verdigris thus formed is known as common verdigris, and consists of three basic acetates of copper, the most basic having a bluish tint, whilst the least basic is green. Its average composition is copper oxide, 43 per cent.; acetic acid (anhydrous), 29 per cent.; and water, 28 per cent.; which corresponds with the formula $Cu(C_2H_3O_2)_2CuH_2O_25H_2O$. Verdigris is also now produced in England and elsewhere by a modification of the above method, in which pieces of flannel dipped in weak acetic acid are used in place of the grape marcs.

Verdigris has but a pale greenish-blue tint, which it soon loses on exposure to light, and it is most readily

blackened by sulphuretted hydrogen; for these reasons verdigris is a very undesirable pigment.

Distilled verdigris is the real and neutral acetate of copper formed by dissolving copper or its oxide in acetic acid, and allowing the salt to crystallise out; the dark green crystals are too transparent to be used as a pigment, but have some use as a glazing colour.

Mountain green is a native carbonate of copper, termed malachite; briefly it differs in composition from mountain blue (see p. 68), the formula being $CuCO_3,CuH_2O_2$. This green is more permanent than any of the artificial copper greens.

Cobalt green is prepared by moistening zinc oxide with cobalt nitrate, then drying and heating the mass to a high temperature; it is a compound of the oxides of cobalt and zinc. This green is quite permanent, but it is rarely used, owing to its high price.

Terre verte or green earth is a natural product found in pockets or veins in igneous or metamorphic rocks in many parts of the world. Terre verte is prepared for use as a pigment by hand-picking, grinding, and levigating, in a similar manner to the ochres (pp. 110 and 111), which it resembles in its properties. Terre verte consists principally of silicate of iron, but contains also notable quantities of magnesia, potash, and soda. It does not appear to have a definite composition, but is an alteration product formed by weathering in the rocks in which it is found. Terre verte is a very permanent green pigment, not affected by other pigments nor affecting them; it is but a dull green and somewhat transparent.

Royal greens are extensively used by coach painters and railway companies on account of their brilliancy, durability, and covering properties. They are not, like Brunswick green, easily affected by atmospheric influences, but retain their colour for a great length of time, especially when coated with a good copal varnish. In preparing these greens, palest and clearest zinc chromes, and Brunswick or Prussian blues are mixed in variable proportions according to the desired depth of colour. Celestial blue may also be used. Royal greens may be prepared from the colours in their dry state by grinding or mixing them under an edge-runner mill, or by mixing and grinding them

when in their pulp state, afterwards drying them in a stove. The latter gives the best and most uniform results.

When it is required to test a pigment for arsenic—so many green pigments contain this dangerous poison, and so have but a restricted use—Marsh's test is very convenient. The apparatus used is shown by Fig. 34, and consists of a gas generator A, a wash bottle B, and a piece of glass tube C drawn to a fine point. A little water is first placed in the wash bottle B, then the pulp colour is placed in the generator A along with dilute sulphuric acid and

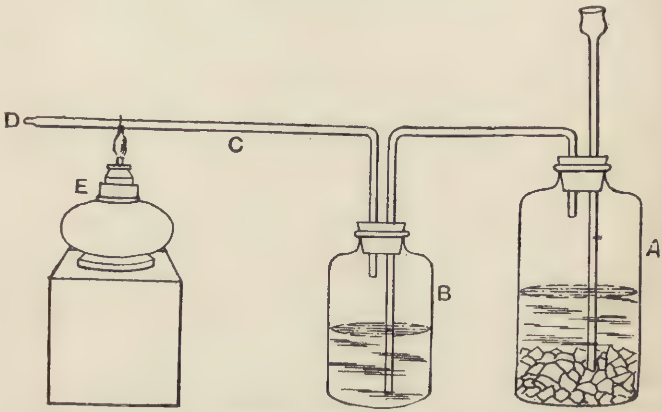


Fig. 34.—Apparatus for Detecting Arsenic.

some sticks of zinc (free from arsenic); hydrogen is evolved, and if arsenic is present this is accompanied by arsenic hydride (AsH_3). When the air in the apparatus is replaced by hydrogen, a light is applied to the end of the tube C at D, where the hydrogen will burn. A small flame E is now placed beneath the tube, and should arsenic be present the hydride will be decomposed by the heat, and a mirror of metallic arsenic will appear in the end of the tube. The test is a very delicate one, a mere trace of arsenic soon yielding a perceptible deposit.

CHAPTER VIII.

RED PIGMENTS.

RED lead is an extensively used fine red pigment, prepared from metallic lead. It was known to the Greeks and Romans under the name of minium, a name applied by them indiscriminately to both red lead and vermilion.

In the preparation of red lead there are two stages: in the first the lead combines with one atom of oxygen, forming lead oxide, plumbic oxide, or massicot (PbO), the last-mentioned word being sometimes spelled masticot.

$$\underset{\text{Lead}}{Pb} + \underset{\text{Oxygen}}{O} = \underset{\text{Lead monoxide.}}{PbO.}$$

Then a further addition of 1 atom of oxygen to 3 molecules of lead oxide forms red lead or triplumbic tetroxide (Pb_3O_4).

$$\underset{\text{Lead oxide}}{3\,PbO} + \underset{\text{Oxygen}}{O} = \underset{\text{Red lead.}}{Pb_3O_4.}$$

Calculated as previously described, 1 atom, or 207 parts, of lead will form 228 parts of red lead.

Red lead is manufactured by one process only—namely, the oxidation of metallic lead in a kind of reverberatory furnace. The furnace (Figs. 35 and 36) is rectangular, arched above, and entirely closed; the bed of the furnace is divided into three sections by very low walls of firebrick, and is provided with three doors in the front, the centre one for charging purposes, and those at the sides for stoking. The centre door has an opening at the top to allow the fumes to escape into a chimney placed directly above. The fires having been lighted, a charge of about 25 cwt. of pig-lead is thrown on to the hearth of the furnace, which is kept at a low red heat—just sufficient to melt the lead. The molten metal is rabbled about with a paddle to bring it in contact with the oxidising flame, and as fast as the oxide is formed it is pushed to the back of

the furnace; more lead is added from time to time, and, when sufficient oxide has been produced, any lead remaining unaltered is removed, and the oxide raked out. The oxide or massicot is next ground and levigated with water. The fine powder thus produced is dried, and again heated in a somewhat similar furnace, in which oxidation is carried a step farther. From time to time samples are examined, and when the desired colour is obtained the mass is raked out.

If after rabbling the molten mass to hasten the oxidation, the temperature is allowed to rise still further, the "dross" will melt or fuse, and litharge will result, which is of no service for making red-lead.

Red-lead is a very bright pigment with a slight orange hue; it is, like vermilion, extremely heavy, the specific gravity being about 8·6. It has good body and covering power, but is blackened by exposure to air containing sulphuretted hydrogen; it is not suitable for the use of artists, but as a common pigment it is very largely employed. It is a powerful oxidising agent, and therefore is an active drier.

Orange-lead is really another form of red-lead, somewhat brighter in colour than the common variety; it is prepared by calcining white-lead.

Other red pigments may now be discussed.

The native pigments are mostly derived from mines in various parts of the world. The most important of these are the oxide reds and Indian reds, ochres, umbers, sienna, and asphaltum, and cappagh browns. There are a great many others, which, however, very rarely come into practical use for painting and decorating.

The natural oxide reds are found chiefly in Cornwall and Derbyshire, in small quantities and of a great many shades. They are the most permanent pigments used by the painter, and are sold under a great many names—as, Indian red, Turkey red, scarlet oxide, Spanish brown, purple brown. In preparing the oxide for use, it is first broken into small pieces with a hammer, and then placed under an edge-runner or grinding mill, where it is crushed into a powder, after which it is passed through a fine sieve (ten meshes to the inch). It is next placed in large wooden tubs, mixed into a pulp with water, and then

passed several times through a pair of flat levigating or grinding stones, until it is quite free from grit. It is then placed in large stone or wood becks, so as to allow the oxide to settle, the usual time being about six or seven days, after which the water is run off. The material is then taken out and placed in drying kilns previous to being manufactured into paint.

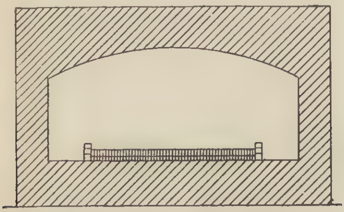


Fig. 35.—Cross Section of Red-lead Furnace.

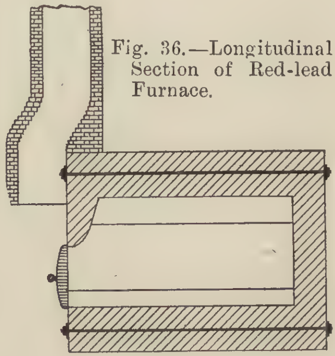


Fig. 36.—Longitudinal Section of Red-lead Furnace.

Following are analyses of a few samples of Derbyshire oxides and reds:—

	Venetian Red.	*Indian Red.*	*Purple Oxide.*
Silica SiO_2	1·03	1·39	1·02
Ferric oxide Fe_2O_3	30·56	93·63	83·02
Magnesia MgO	69	—	—
Water	1·01	38	8·31
Hygroscopic water	14·05	—	7·65
Calcium sulphate $CaSO_4$ ..	52·59	4·59	—
	99·93	99·99	100·00

The artifical oxides are made chiefly by the two following processes: (1) By heating or calcining green copperas $FeSO_4 7H_2O$. The depth of colour depends on the length

of time the copperas is calcined, and the various heats to which it is subjected. For instance, if an oxide of a light shade is required, a low heat is maintained; while for a deep oxide a cherry-red heat is necessary, and for a purple oxide or rouge a white heat. The after-treatment is much the same as that of the natural oxides. (2) By heating or calcining ochres. The plant for this process is less costly. The ochre is first ground to a fine powder under an edge-runner mill, then mixed into a pulp with water and passed through levigating stones until it is quite free from grit, when it is placed on a stove to dry, after which it is placed in a calcining oven; the depth of colour depending on the time occupied in calcining—the deeper the colour, the longer the time required. Light reds are usually made by this process.

Under the heading of iron reds it is convenient to group several pigments which contain ferric oxide (Fe_2O_3) as the true colouring matter. A number of well-known and largely used pigments are known as red oxides; these red oxides are formed largely from minerals, such as red hematite, brown hematite, ochre, etc., by the processes of grinding, roasting, and levigating, and they are also formed from the salts of iron. The minerals are roasted in reverberatory furnaces, which, though they differ in details, work upon the same principles as the red-lead furnace (Figs. 35 and 36), this roasting serving to drive off water and other volatile matter, and to destroy any iron pyrites present. The roasted mineral is then ground under edge-runners and levigated in tanks on the principle shown by Fig. 40 (p. 113), the finer pigments only being collected for use, and the remainder returned to be ground still further. As a final treatment, the pigment is dried on shelves in a heated chamber.

Pigments are also produced from the salts of iron. For instance, by heating ferrous sulphate ($FeSO_4 7H_2O$) in retorts during the preparation of Nordhausen sulphuric acid, a red oxide of iron is formed, known as colcothar or rouge, and by varying the temperature at which the roasting is carried out, it is possible to modify the colour of the resulting product considerably, the lower the heat the brighter being the red; at a white heat the product is of a purplish colour, and is known as purple brown.

In the preparation of red oxides a great many waste liquors containing iron are also brought into requisition. In the extraction of copper from its ores by the wet process, and also in the galvanising of iron, large quantities of waste liquors containing more or less sulphate of iron are produced. At one time these products were run into the sewers, but now they are employed for the manufacture of Venetian red. Lime is added to the liquids, and results in the formation of a precipitate of ferrous hydrate ($Fe(HO)_2$) and sulphate of lime ($CaSO_4$); the precipitate is at first green, but it rapidly oxidises in contact with the air, becoming yellow owing to the formation of ferric hydrate ($Fe_2(HO)_6$). The pigment is collected by filtration, and is washed, dried, and then calcined in the furnace.

The iron reds produced by the several processes described pass under a variety of names, such as red oxides, Indian red, light red, rouge, purple red, etc.; these are in many cases nearly pure oxide of iron, containing from 90 to 99 per cent. of ferric oxide (Fe_2O_3); but red pigments prepared from ochre contain a certain proportion of silicate of alumina or clay, and Venetian red, artificially made, contains more or less sulphate of lime.

All the iron reds are excellent pigments, both for covering power and permanence; though not so brilliant as vermilion (see below), they are still very fine pigments, and their permanence is shown by the paintings of the ancient Egyptians, who used a native iron red very largely. These reds are equally as good in distemper as in oil, and are unaffected by exposure to light, to air, or moisture and foul gases.

Red oxide is a very difficult pigment to test with acids, etc., unless its origin is known, as its solubility varies according to its composition and preparation. The simplest method is to weigh out a given quantity into a beaker, and add a mixture of hydrochloric and nitric acids, and heat, until completely decomposed, over a Bunsen burner. Then evaporate the solution to dryness, and treat the residue with dilute hydrochloric acid, then wash well with water, filter, and finally dry. This process will leave the adulterants, barytes, silica, etc.

Vermilion, an extremely fine pigment, is a sulphide of mercury (HgS), and it occurs native as cinnabar, constituting

the principal ore of the metal mercury. Cinnabar in the massive state is of a black or violet red colour, but when it is crushed to a fine powder it is found to have a crimson red colour, and it was in this state at one time used as a pigment.

Vermilion is produced artificially by many processes, which do not differ essentially from one another. In certain of these processes (known as the Dutch, Chinese, and other methods), the sulphide of mercury is sublimed; these are known as "dry methods." In the remaining processes, certain solutions are employed for producing the colour, and they are therefore known as "wet methods."

In the dry methods of preparing vermilion 42 parts of metallic mercury and 8 parts of sulphur are triturated or heated together, the black substance thus formed being known as "æthiops." The æthiops is transferred to large deep iron pans set in rows in a furnace, the pans being covered with iron rings or hoods, in the centre of which are the charging holes. The furnace being in proper condition, a charge of æthiops is thrown into each pan, and results in the production of a large flame of burning sulphur at the charging hole. When this flame dies down another charge is introduced, and the process is repeated several times, the whole operation occupying about thirty-six hours; the furnace is then allowed to die out, and as soon as the pots are cold the covers are removed. The sublimed sulphide of mercury is found as a thick blackish-red mass adhering to the covers; it is removed, broken into small pieces, and very carefully ground. The ground vermilion is boiled with a little caustic potash, then well washed with hot water, and dried. The result of the sublimation and grinding is the conversion of the black sulphide of mercury or æthiops into the red sulphide or vermilion. There is no change in the chemical composition of the substance, the alteration in its properties being due to a physical change or rearrangement of the molecules; the black sulphide is amorphous—that is, without form—whereas the red sulphide is crystalline.

The many different wet processes of preparing vermilion differ only in detail, and depend, like the sublimation methods, upon the conversion of the black into the scarlet modification of the sulphide. The black sulphide of

mercury is first formed by triturating together 100 parts of mercury, 38 parts of sulphur, and water until the two elements combine. The product is then mixed with a dilute solution of caustic potash, and heated for several hours at a temperature not exceeding 50° C. The colour of the compound gradually changes, appearing first brown and then red; when a full scarlet colour is developed, the heating is stopped, and the product thoroughly washed with cold water. The material formed in this way is fully equal to that produced by sublimation.

Vermillion is one of the heaviest pigments used, the specific gravity being about 8·0 to 8·2; it has a brilliant scarlet hue, and has good body and covering power; it is usually considered to be a very stable pigment, but under the direct rays of the sun it gradually becomes black, returning to the amorphous sulphide, as shown by the experiments of Prof. Rood, and Dr. Russell and Capt. Abney. Owing to the high price of vermilion, it is liable to be adulterated with the cheaper red pigments.

A mixture of ultramarine and vermilion in roughly equal proportions gives a reddish purple pigment, but the resulting shade will depend largely on the quality of the ultramarine used, and on its strength and purity.

Vermilionette is distinct from vermilion, for which it is used to some extent as a cheap substitute. It is partly a lake colour, and is formed from the coal-tar derivative, eosin (see p. 83). To obtain the desired shade, the lake is precipitated upon orange lead. A solution of the eosin colour is mixed with certain proportions of orange lead and barytes, which are kept in suspension in the fluid while the dye is being precipitated by the addition of a solution of acetate or basic acetate of lead; the colouring matter is then allowed to settle out, and is washed and dried in the usual manner.

Vermilionette is, therefore, a mixture of orange lead and barytes tinted with eosin. It generally is a very brilliant pigment, and possesses good covering properties, but it does not resist exposure to light and air, and therefore cannot be recommended for outside work.

In determining whether a sample of colour is a vermilion or a vermilionette, it must first be remembered that vermilion is a very stable pigment, practically unacted upon

by alkalies or acids (except aqua regia), but vermilionette is not so stable. The pigment should be treated with strong nitric acid, the liquid diluted and filtered; vermilion will be unacted upon, but vermilionette will become brown, and the filtered liquid, on addition of hydrochloric acid, will yield a white precipitate of lead chloride soluble on boiling, but re-precipitated on cooling as a crystalline powder. A portion of the colour should be treated with aqua regia, when vermilion will dissolve entirely, but vermilionette leaves a white residue; the liquid should be diluted, filtered, and the precipitate washed with hot water, dried, and fused with carbonate of soda. The fused mass should be treated with acidified water; and barium chloride added will yield a white precipitate due to a sulphate; the residue, insoluble in water, on acidifying and adding dilute sulphuric acid will yield a white precipitate showing the presence of barium; thus barium sulphate will be detected. Should there be no residue on treating the colour with aqua regia, then the pigment is vermilion, and sulphur may be detected by taking a portion of the solution and adding barium chloride; a white precipitate will indicate a sulphate formed by the oxidation of the sulphur. Mercury will be found by evaporating some of the solution to dryness, dissolving the residue in water; on adding stannous chloride to this, a grey precipitate of metallic mercury will separate out.

A very simple test to distinguish vermilion from vermilionette is to place a small portion in a porcelain dish over a Bunsen burner; in a few minutes vermilion will entirely sublime, but vermilionette leaves a bulky buff-coloured residue. A further help is to remember that vermilion slowly blackens on exposure to direct sunlight, the change being due to an alteration in the physical properties of the mercuric sulphide, crystalline or red sulphide changing to the amorphous or black sulphide; whereas vermilionette on exposure loses its brilliant tint very quickly, due to the fading of the eosin.

CHAPTER IX.

BROWN AND BLACK PIGMENTS.

CHIEF among the brown pigments are the umbers which are found native in many parts of the world. Large quantities are obtained in Wales, Cumberland, and Derbyshire, as well as in the United States, in Italy, and in Asia Minor. The Turkey umbers, famous for their deep-staining brown tint, are from Asia Minor. The umbers from the Cumberland and Derbyshire mines are of a soft reddish-brown tint, whilst Wales yields an umber of a light yellowish-brown tint, having very little staining power.

The burnt Turkey umbers are distinguishable from the raw umbers by a finer and deeper staining warm brown tint. The burnt umber is prepared by calcining the raw at a cherry-red heat for about five hours, finishing the process in much the same way as when dealing with the natural oxides (see the chapter on red pigments, pp 96 to 99).

Following are analyses of samples of umbers:—

	Cumberland.	*Asia Minor.*	*Derbyshire.*
Barium sulphate $BaSO_4$	33·305	29·005	1·480
Calcium carbonate $CaCO_3$	3·708	6·660	4·589
Alumina Al_2O_3	4·083	2·500	13·813
Calcium sulphate $CaSO_4$	3·052	1·235	2·005
Ferric oxide Fe_2O_3	25·300	30·400	28·503
Manganese MnO_2	10·525	12·360	6·100
Silica SiO_2	3·430	29·666	26·018
Water, hygroscopic	10·300	9·450	5·511
Water combined	6·350	8·325	11·351
	100·053	100·596	99·370

At Iskanderun, Asia Minor, whence the samples tabulated in the second column of figures were taken, there was found not long ago, 12 ft. below the level of the ground, a layer of umber 33 ft. in thickness. This is one of the largest finds yet made.

The names umber and brown ochre are applied to many pigments having a brown colour and resembling the ochres more or less in their properties and composition. These pigments occur naturally in Derbyshire, Cumberland, Devonshire, Cornwall, etc., and also in many localities abroad. They are mined and prepared for use as pigments in a similar manner to the ochres.

In composition the umbers and brown ochres very much resemble the yellow ochres, as they consist essentially of ferric hydrate, $Fe_2(HO)_6$, with more or less clay, sand, etc. In addition, umber contains a rather large amount of manganese, probably existing in the form of hydrated manganese dioxide, $Mn\ (HO)_4$, from which the pigment derives a part of its colour.

Umbers are rich transparent brown pigments, more or less variable in tint, but with a warm or ruddy hue. They are perfectly permanent under all conditions, mix well with other pigments, and, being inexpensive, are largely used. Turkey umber is esteemed the best.

The Vandyke browns usually sold are varieties of peat or mould formed by the decay of vegetable matter. They belong to the class of products, not yet sufficiently understood, known to chemists as "humus," or "humic acid." Vandyke brown is not usually purified before use; hence it often contains fragments of wood, stones, etc.

Vandyke brown is a fine brown colour, but very transparent and exceedingly fugitive. Like most organic pigments, it is a bad drier when mixed in oil; its chief use is as a stain for wood, exactly imitating walnut in appearance. For this purpose it is ground in water or used with an alkali, in which it is soluble. Sometimes a kind of umber is sold as Vandyke brown; this is not dissolved by alkalies, and therefore produces a very poor stain.

Artificial Vandyke brown is now produced by calcining the bark of trees, vines, and different kinds of decayed wood, the chief place of production being Italy, where the vineyards afford a convenient supply of twigs for calcining.

Italian Vandyke brown is of a fine reddish-brown colour, is permanent, and mixes well as a pigment or in pulp for water-colour painting. The following shows the analysis of a sample of Italian vandyke brown :—

Water	2·389
Organic Matter	69·221
Ferric oxide Fe_2O_3	2·005
Calcium carbonate $CaCO_3$	2·485
Silica SiO_2	3·162
Alkaline carbonates	21·009
	100·271

Cappah brown, or cappagh brown, is a native colour much resembling the umbers. It is a permanent colour, and is much used, being sometimes preferred to Vandyke brown owing to its warm brown tint. Originally it was found only in the south of Ireland, but is now obtained in small quantities in several parts of Germany. Below is the analysis of a sample from Frankfort-on-the-Main, Germany :—

Ferric oxide Fe_2O_3	39·012
Manganese dioxide MnO_2	26·126
Calcium carbonate $CaCO_3$	1·002
Silica SiO_2	3·937
Organic matter and water	26·436
Lime CaO	0·255
Magnesium carbonate $MgCO_3$	0·051
Alkaline sulphates	0·009
Alumina Al_2O_3	3·162
	99·990

Cassel earth is an earthy pigment resembling the umbers in its composition and properties, obtained in various tints and shades. The earth is found in thin layers among rocks in various parts of Germany. As a pigment Cassel earth is not to be depended upon ; the colour is not permanent, and the earth varies in composition.

Bistre is a brown pigment, the best quality of which is prepared by washing the soot of beechwood with hot water

until all the soluble matter has been extracted. This is dried, and is then ready for use. The soot may or may not be ground for the purpose. The colour is a fine warm yellowish-brown, whose permanence largely depends on the character of the wood soot in the first case. The greater the quantity of tarry matter contained by the soot the more fugitive is the resultant bistre.

Sepia is used chiefly by artists, but it deserves slight mention here. The cuttlefish (*Sepia officinalis*) has a gland which secretes a brownish-black liquid in an "ink-bag." The ink-bag is carefully removed from the animal, dried, and boiled in a solution of soda to detach the pieces of sac or bag from the actual pigment; this, insoluble in water, is extremely diffusible through it, so that it is possible to prepare the sepia by a process of decanting or levigation. The sediment strained forms into cakes or sticks. Sepia has a very fine texture, mixes well with oil and with water, and has a marvellous covering power even though it is inclined to be transparent. Its property of being so used as a water colour to show a variety of tints and shades gives it great value to artists for monochrome work. It is fairly permanent, only very slightly affected by light and air, and it mixes well with all pigments.

The commercial method of preparing sepia is to boil the ink-bag in water to extract the alkaline salts, and then in dilute hydrochloric acid to remove the carbonates of calcium and magnesium. Having been washed with water, filtered and dried, the sepia is finished. Chemically, it consists of:—

Melanin or black pigment	78·00
Calcium carbonate, $CaCO_3$	10·40
Magnesium carbonate, $MgCO_3$	7·00
Alkaline sulphates and chlorides ...	2·16
Organic mucus	0·84
	98·40

The rest of this chapter will be devoted to black pigments, chief among which is lampblack.

The formation of lampblack by holding a cold object in the flame of an ordinary oil lamp is a familiar illustration of the operation of preparing this pigment. Originally a large oil lamp was allowed to burn under a funnel-shaped

tube connected to a series of cylindrical bags in which the deposit of soot or lampblack collected. This method, however, allows of only a limited production, and it is now more usual to heat the oil up to its firing-point and then allow it to burn with a limited supply of air.

The plant used in the manufacture of lampblack is shown by Fig. 37. It consists of a large rectangular brick chamber, cut up into sections C by dividing walls D in which openings E are left alternately top and bottom. In the first chamber is built a small furnace B, the stoking-hole being outside the chamber. A large iron pan A is fitted in this furnace, and directly over the pan a small pipe is fixed from a tank outside for delivering a slow stream of the oil. A small quantity of oil is first placed in the pan, and highly heated by the furnace. The oil is then set on

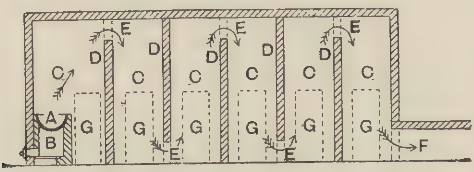


Fig. 37.—Lampblack Chamber.

fire by applying a light, and the chamber closed. The very cheapest oils are used in this process, either waste vegetable or animal oils, or the heavy oils from coal tar. The oil is allowed to drip from the pipe as fast as that in the pan burns away ; the smoke and soot from the burning oil pass through the openings from one chamber to another, finally passing into a chimney through the flue F. In the chambers the lampblack is deposited ; it is swept down from time to time by men who pass in through the doors G G to each chamber.

The pigment known as lampblack is the coarsest part of the black, and is deposited in the front chambers ; the deposit in the rear chamber is much finer, and is usually known as vegetable black.

A very fine kind of black has been produced to some extent in America by burning the gas which escapes from the oil wells and allowing the soot to deposit upon iron

plates cooled by circulating water. The black is scraped off the plates by a mechanical arrangement and packed in barrels. This is the finest black pigment; it is extremely light, and the carriage on such bulky cargo being high it is expensive in Great Britain. It is known as gas black or carbon black, and is used chiefly in the manufacture of fine printing inks.

Lampblack is almost wholly carbon. It is of a fine black colour, has good covering power, and is perfectly stable.

Charcoal black is formed by heating wood in a closed vessel or retort until the whole of the moisture, gases, and volatile matter are driven off; the residue is then carefully ground. Frankfort black is in this manner prepared from the twigs of the vine, peach-stones, etc. Charcoal blacks are, like lampblack, composed almost entirely of carbon; Frankfort black is a good black, but the other varieties are not of much value as pigments.

Drop black is lampblack ground with water; it contains carbon only, and is therefore not acted upon by acid.

Ivory black is made by submitting waste pieces of ivory, such as turnings, etc., to heat in a closed crucible. Water, gases, etc., are given off, and the ivory is reduced to charcoal. It is left over the fire for about half an hour after it is found that smoke discontinues to pass from it. The material is then a hard, carbonaceous matter which must be pounded and ground on porphyry with water, washed with warm water and then dried. A final grinding renders it suitable for use. It forms a fine black pigment, but is not a pure carbon like that produced from vegetable matter, as it contains more or less phosphate of lime.

Bone black has now almost entirely superseded ivory black, the material from which the latter is obtained being so scarce. Bone black is produced by heating animal bones in closed crucibles set side by side in a large furnace, or by using large fire-clay or iron retorts which allow of the collection and utilisation of the gases, ammonia, and tar, which are formed by the destructive distillation. The black formed from bones contains only a small percentage of carbon (from 10 to 12 per cent.), the chief constituent being phosphate of lime (from 65 to 72 per cent.), with smaller amounts of carbonate and sulphate of lime. Bone black is a greyish-black pigment, but quite permanent.

Bone black is used very largely for decolorising sugar, etc., and after it has served for this purpose it is revivified by again heating. This operation may be repeated several times, but finally the pores of the black become choked, and it is no longer of use to the sugar refiners. In this condition it is thoroughly heated, resold as "spent" black, and occasionally finds its way to the painter. Spent black is of good quality, but contains more carbon than the new bone black, from 18 to 24 per cent. instead of from 10 to 12 per cent.

Both new and spent bone blacks are sometimes known as animal blacks, but the latter name is also applied to blacks made by heating all kinds of waste animal matter, such as hoofs, horns, etc., materials which yield very variable products.

Ivory black, the deepest and purest of the blacks, being somewhat hard, requires very careful grinding, and unless ground very fine is useless. It is best ground in turpentine, and diluted for use with turpentine, gold size, and a little varnish.

CHAPTER X.

YELLOW AND ORANGE PIGMENTS.

SOME of the most valuable yellow and orange pigments are the lead and zinc chromes, whose preparation is described minutely in Chapter V. (see pp. 69 to 79). Some of the lakes (see p. 84) also are included by the heading of this chapter. Lemon chrome is referred to on p. 79.

Yellow ochre occurs naturally in many parts of the world; in Great Britain excellent ochres are found in Oxfordshire, Derbyshire, Cornwall, and other counties, also in Wales and in Ireland. Yellow ochre usually occurs in veins or masses, and is mixed more or less with "gangue" or vein stuff, from which it has to be separated. The ochres as they are raised from the mines occur in large pieces, which require to be pulverised and levigated in order to remove the particles of grit and other impurities which they usually contain. In certain cases the ochre is sufficiently soft to fall to powder by simply washing with water; but if not, it may previously be ground in an edge-runner mill or in a special form of disintegrator.

The Niagara crusher and pulveriser (Fig. 38) is shown in section by Fig. 39. It consists of a drum A which is capable of being revolved; the walls of the drum are of hard iron, built up in segments J, and each one is replaceable when worn. E is a crushing roller keyed on to the shaft G, and weighted by a heavy spring H. I I are buckets fixed to the drum on each side of the crushing roller for the purpose of elevating the material undergoing crushing, and bringing it time after time to the front of the roller. (L shows line of resistance.) The rock to be crushed is fed in through the hopper, and the finely powdered material is carried by a current of air into either a chamber or bags. O shows the outlet. There are many other forms of crushers; the one illustrated will, however, serve as a typical example.

The pulverised ochre is next placed in a large tank A (Fig. 40), through which a gentle current of water is allowed to flow, carrying with it the lighter particles of ochre but leaving the impurities, which have to be cleared out from time to time; the ochre suspended in the water passes on to the next tank B, in which a part is deposited, and so on through the series, the finest ochre being found in the last tank of all. When the pigment has collected in sufficient quantity, it is dug out and removed to a drying shed, the floor of which is heated by steam pipes—the drying of the pigment being performed at as low a temperature as is practicable.

The ochres have a variable composition, and are simply clays coloured more or less by the hydrated peroxide of

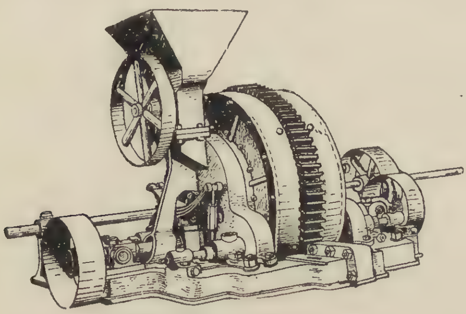


Fig. 38.—Niagara Pulveriser.

iron. A sample of Oxford ochre had, according to Professor Church, the following composition:—

Hygroscopic mixture	7·1
Combined water	9·0
Ferric oxide	13·2
Alumina	6·3
Silica	61·5
Calcium sulphate	1·4
Undetermined	1·5
	100·0

Yellow ochre is a very cheap and useful pigment, of good body and covering power, and quite permanent under

all conditions, either in oil or in water. The hue of the pigment varies considerably from a pure yellow to a reddish or brownish yellow, this variation being partly due to the amount of combined water, as also to the presence of ferric oxide.

According to Professor Church, yellow ochre contains three hydrated oxides of iron, known to mineralogists as limonite ($2Fe_2O_33H_2O$), xanthosiderite ($Fe_2O_3H_2O$), and bog-iron ore ($Fe_2O_33H_2O$). The colouring power of the pigment depends upon the amount of iron present, the silicate of alumina or clay acting as a diluent. But the quality of an ochre is not dependent upon its composition;

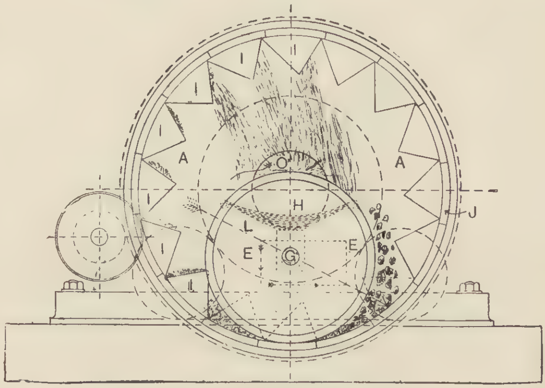


Fig. 39.—Section of Niagara Pulveriser.

this is solely judged by the hue, the variety known as "golden" ochre being much esteemed.

Raw siennas are merely varieties of yellow ochre having a peculiar brownish-yellow colour. Yellow ochres are usually produced by the direct oxidation of ores containing iron, particularly iron pyrites (FeS_2), and they are accompanied by portions of the unaltered minerals and also more or less "vein stuff," such as quartz, etc. The siennas, on the other hand, have been formed by deposition from water, and occur in hollows or pockets; they are remarkably free from extraneous matters.

By heating yellow ochre, pigments of many different

shades of red, brown, and purple are obtained; many of these have already been dealt with.

Raw sienna also yields, on heating, a rich reddish pigment known as "burnt" sienna.

Gamboge, a yellow gum resin, is imported in rolls, pipes, and cakes from Siam, Ceylon, and India. The pipe gamboge is the product of the tree known as the *Garcinia morella;* it is melted, and cast in the hollow stems of the bamboo. When pulverised and mixed with oil, it gives an amber yellow pigment, which soon fades. Gamboge consists principally of two constituents, a gum soluble in water and a resin soluble in alcohol, the latter being the true colouring matter. For painting purposes gamboge is simply pulverised. With water it forms a milky yellowish fluid. Gamboge forms a transparent amber yellow pigment with oil, but it is not permanent.

Naples yellow is an antimonial pigment which has been

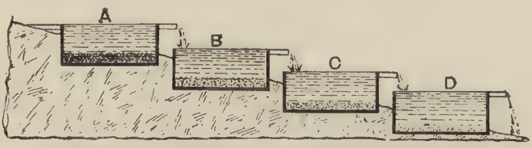


Fig. 40.—Pigment-precipitating Plant.

in use for a considerable time. The finest product is made by calcining in a crucible a mixture of tartar emetic (antimony, potassium tartrate), lead nitrate, and common salt. The soluble salts are then washed out with hot water, and the pigment is dried. Naples yellow is a basic antimoniate of lead. It has a very good body and covering power, and it is quite unaltered by sunlight; foul gases blacken it, this change taking place very quickly if the pigment be used as a water-colour.

The true Naples yellow is prepared for artists' use only, and has but a limited application; there are, however, several spurious Naples yellows which contain cadmium yellow or chromate of lead mixed with a white pigment.

Cadmium yellow is a very fine yellow pigment obtained by passing a current of sulphuretted hydrogen gas through a solution of cadmium salt, either the chloride or sulphate. The metal cadmium was discovered in 1817. It accom-

panies the ores of zinc, especially those occurring in Silesia, and being more volatile than zinc, rises first in vapour when the calamine or zinc ore is subjected to distillation with charcoal.

Cadmium yellow is the sulphide of the metal cadmium (CdS). For the purpose of the artist, it is prepared by passing sulphuretted hydrogen gas through a solution of cadmium chloride or cadmium sulphate, as has been said. The reaction is shown in the following equation:—

$CdCl_2$	+	SH	=	CdS	+	2HCl
Cadmium chloride.		Sulphuretted hydrogen.		Cadmium sulphide.		Hydrochloric acid.

The apparatus used in the preparation of cadmium yellow is shown by Fig. 41, where A is the generator for sulphuretted hydrogen, which is produced by the action of hydrochloric acid upon sulphide of iron. The gas passes from the generator through several Woulff's bottles B C D containing solutions of the cadmium salt; in these the pigment is precipitated, and as soon as it is all down, the liquid is filtered, and the cadmium yellow, thoroughly washed with hot water to free it from soluble salts, is then dried in a hot-water oven. Professor Church recommends a final treatment with carbon bisulphide, to remove any free sulphur which might be present and which would be injurious.

Cadmium yellows may be obtained of many tints, according to the conditions of the precipitation. Pale yellows are produced by working with the solutions neutral and as cold and dilute as possible; on the other hand, reddish orange varieties are obtained when the liquids are hot and acid. The different varieties of this pigment appear to have identically the same composition, the only difference being in their physical structure.

This pigment is much used by artists, as, under the influence of light, moisture, or foul gases, it remains unaltered; it mixes well with other pigments, excepting those containing lead or copper, with which it reacts, forming black sulphides of those metals. The price of cadmium yellow being rather high, it is liable to be adulterated, or even entirely replaced by cheaper yellow pigments.

King's yellow, or Imperial yellow, a beautiful yellow pigment used by the ancient Egyptians and the Romans,

is a sulphide of the metal arsenic (As_2S_3). This pigment may be prepared in a similar manner to cadmium sulphide —by passing a current of sulphuretted hydrogen through a solution of white arsenic (As_2O_3) in hydrochloric acid.

As_2O_3	+	$3H_2S$	=	As_2S_3	+	$3H_2O$
Arsenious oxide.		Sulphuretted hydrogen.		Arsenious sulphide.		Water.

It is washed and dried as previously described. Several other methods are used for preparing this substance. It is largely produced by heating together in a crucible a mixture of white arsenic and sulphur, the sulphide subliming into a hood placed over the crucible; the material is then ground and washed.

King's yellow is of good colour and body, but it fades rapidly. Besides other defects, it usually contains unaltered white arsenic, and is thus extremely poisonous. The defects mentioned are sufficient to condemn it for use as a pigment.

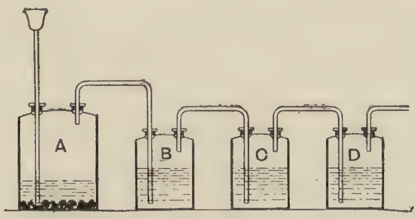


Fig. 41.—Apparatus for Preparing Cadmium Yellow.

Cobalt yellow or aureolin is the name applied to a double nitrite of potassium and cobalt which has the composition $K_6Co_2(NO_2)_{12}$. (Cobalt is a white, brittle, very tenacious metal, having a specific gravity of 8·5, and a very high melting point. It is strongly magnetic.) The pigment is prepared by adding carbonate of potash to a solution of cobalt nitrate, then acidifying with acetic acid and adding a strong solution of potassium nitrite. The pigment requires a short time to form. Aureolin is a fine yellow pigment, but is crystalline and somewhat transparent.

Mars yellow contains iron like the ochres, which it resembles to some extent, but it is produced artificially

Solutions of ferrous sulphate (copperas, $FeSO_4$) and alum are mixed and precipitated with carbonate of soda or lime; the precipitate is at first dark green, but on exposure to air, or by blowing air through the hot liquid, it becomes yellow.

Indian yellow is a peculiar yellow product made in India from the urine of cows fed upon the leaves of the mango tree. This food increases the secretion of the bile, and the excess passes into the urine, to which it imparts a strong yellow colour. One authority states that the pigment is supposed to be the earth dug up from the stables where cows have been housed during the winter and fed in the manner described, and that the crude pigment is imported in the form of balls, from 3 in. to 5 in. in diameter, having an offensive urinous odour. The balls have to be washed and levigated. Hurst says that the urine is itself collected and boiled down in earthern vessels to precipitate the yellow, this being gathered on calico and made into balls, the total yearly production of which is only about 100 cwt. or 120 cwt. The pigment is fairly bright, has good covering power, is non-poisonous, but soon fades in the sunlight. Probably it is a compound of magnesia and a peculiar acid known as euxanthic acid, though potassium benzoate and other bodies are also present.

CHAPTER XI.

BRONZE COLOURS.

As substitutes for thin films of the genuine metal, paints resembling gold, silver, bronze, etc., have long been widely employed. These paints are formed by mixing what is known as metallic bronze with a suitable medium which may be one out of, say, twenty liquids. A few of these are gum water, copal varnish, white spirit varnish, a mixture of turpentine and French polish, and a solution of collodion cotton in amyl acetate diluted with petroleum ether.

In the olden time, should a little gold paint be required, it was the usual practice to take a little gold leaf and to mix it with a little honey or gum-water and grind it with the muller on a marble slab or sheet of glass until it was reduced to a powder. The honey or gum-water was then washed out with water, and the gold powder thus obtained was dried and could then be mixed with any medium desired for the manufacture of a gold paint. If a pure gold leaf is ground up in this way the result is, of course, a pure gold paint. The present gold paints do not contain a particle of gold, it being a great deal too expensive for this purpose.

In a similar way silver powder was produced from silver leaf and formed a very fine white metallic pigment. The silver bronzes are, however, made from other and cheaper materials than silver at the present time; a pure silver bronze is not often obtainable.

The bronze colours now employed are principally copper-tin or copper-zinc alloys—that is to say, they are composed either of bronze or of brass, and they are for the most part made abroad.

The cities of Fuerth and Nuremberg, in Bavaria, are the centres of the bronze colour industry, and from these places the colours are exported to all parts of the world. The

alloy is cast into rods about $\frac{1}{2}$ in. diameter and about 3 ft. long. The rods are rolled out until they are about 2 in. wide, then cut up into short pieces. These pieces are separately beaten with a hammer; they are then washed in dilute sulphuric acid to remove impurities and dirt, and, after drying, are beaten still further under a steam hammer until they are reduced to thin films. These are cut up by shears. The metallic clippings are next taken to the stamp mills, which work in a series. In the stamp mills the clippings are quickly reduced to powder. The next operation is sieving, whereby different grades of powder are obtained. The heavier powders are usually the best; the lighter portions are usually adulterated and sold cheaply.

To obtain increased lustre in these powders, they are often put through a steel cylinder in which are revolving steel-wire brushes, which serve to polish the powders.

The colours of the bronze powders, of course, vary with the composition of the alloys from which they are made, and it is possible to get quite a range of colours. There are, however, several methods by which bronze powders may be coloured. Heat is a well-known agent for the production of colours on metals; this it does by the production of thin films of oxide. Baths of different materials are used for heating, such as a mixture of oil and vinegar, paraffin wax, and oils containing sulphur.

Another method of colouring bronze powders is by submitting them to the action of sulphuretted hydrogen in a closed chamber, when a thin film of sulphide is formed. This is sometimes followed by heating. A bath of chloride of tin also yields pale bronzes. Many of the brilliant coloured bronzes are now made by dipping the metallic bronze powder in an alcoholic solution of an aniline colour and allowing to dry. A very thin film of the colour is thus left upon the bronze. It is also stated that inferior bronze powders are prepared by coating zinc powder with brass by immersing it in a mixed cyanide of copper and zinc solution, keeping the powder in motion while the deposition is taking place.

Fine copper bronzes are made from pure copper, which is obtained by reducing finely powdered copper oxide in a current of coal gas or petroleum vapour, this being done in a tube heated by a furnace.

Pale gold bronze is a mixture of 54 copper and 11 of zinc. Red tones are produced by adding more copper. Dutch leaf has 20 to 30 per cent. of zinc and from 70 to 75 per cent. of copper, and is sometimes ground with real gold to produce bronze powder. French leaf has more zinc, is harder and is of a purer yellow. Florence leaf has still more zinc. White leaf is principally tin. The fragments from the manufacture of these metals are pounded, then brushed through sieves, ground in gum water on marble slabs for six hours, sorted, and dried.

The following is a cheap gold bronze. Grind and make into a paste with oil, verdigris 8 oz., tutti powder (flower of zinc) 4 oz., borax and nitre 2 oz. each, corrosive sublimate 2 dr. This is fired and, when cold, rolled into leaves, being afterwards ground to powder.

A very simple way of making gold bronze is to sprinkle powdered tin into very dilute sulphate of copper. This will throw down some finely divided gold-coloured bronze. To make a red bronze, add pulverised red ochre or a solution containing chloride of antimony and sulphate of copper—12 to 20 parts of copper and 1 of tin.

One red bronze is made thus:—Heat sulphate of copper 100 parts, with carbonate of soda 60 parts, until it becomes a mass; when cold, powder, add copper filings 15 parts and again well mix. Maintain at a white heat for twenty minutes, and when cold reduce to an impalpable powder, wash, and dry.

To make a copper bronze, plunge a plate of iron into a hot solution of sulphate of copper; the fine scales of copper thrown down are repeatedly washed with water, and mixed with six times their weight of bone dust.

Other alloys besides those mentioned are sometimes employed in the manufacture of bronze paints; for instance, aluminium bronze is sometimes used. Lehmann makes bronze powders from an alloy of copper containing 10 per cent. of aluminium and ·05 to 1 per cent. of bismuth. This may be converted into vari-coloured powders by varying the amount of aluminium, and also by oxidising it by heat.

Aluminium powder is used as a silver bronze. Amalgams also have been proposed as bronze powders, a gold bronze powder being made by melting together 83 parts of

copper, 17 parts of zinc, and adding mercury. When cold the mass is brittle, and may be reduced to powder. A silver bronze of this class is made by treating equal parts of bismuth, tin, and mercury in the same way.

A method of making silver bronze is to melt together 1 oz. each of bismuth and tin. When tin is heated above melting point in contact with the air it becomes a yellowish-white powder, and volatilises at a white heat. Add from 1 oz. to $1\frac{1}{2}$ oz. of quicksilver, and when cold pulverise the alloy. To make dark olive-green bronze, add muriatic acid and arsenic to a mixture of orange bronze.

To give some idea as to the range of colours in which it is possible to produce bronze powders, it may be mentioned that the Japanese make dark brown powder approaching black with oxidised iron; deep warm brown by different proportions of the same material; light brown with bronze; deep red with copper. They mix iron, gold, and silver, and get a blue by means of steel. Another colour is produced with equal parts of gold dust, vermilion, and charcoal. Plumbago is used to produce a black powder.

Of the substitutes used in place of bronze powders, one very brilliant example is called mosaic gold; it is really a sulphide of tin formed in a special manner.

Another substitute made by an American firm is powdered mica coloured with coal-tar dyes; powdered tin is also coloured by these dyes and sold. Tin in a very fine state of division, suitable for this purpose, is made near Breslau. The tin (or turnings of tin alloys, as gun-metal) should be heated with hydrochloric acid; the tin dissolves as chloride. The lead contained in the metal precipitates as chloride on cooling and is filtered off; the solution, containing the tin, is treated with scrap zinc; this causes the deposition of the tin as a sponge; it is washed and dried. It is sold under the name of "argentine."

CHAPTER XII.

DRIERS.

It is not quite clear as to what constitutes a drying oil, or as to what is formed when an oil dries. Linseed oil is the oil most largely used by painters, and, for general purposes, it is the best drying oil; it dries more quickly and more effectually than any of the other oils, with one possible exception, that is walnut, which is stated by some to dry as quickly. The other drying oils are poppy, camelina, sunflower, nut, hemp, and pumpkin-seed oils. Several other oils dry to a slight extent, but so slowly and imperfectly that they are of no use whatever to the painter. They are employed to some extent to adulterate, and at the same time to spoil, the drying oils. These are sesame, cotton-seed, earth-nut, and rape-seed oils.

Linseed oil is a good example of the drying oils, and, as described in Chapter I., it is extracted from linseed; which is the seed of the flax plant (*Linum usitatissimum* and *L. perenne*. It has a golden-yellow or brownish colour, according to its quality. When linseed oil is exposed to air it becomes gradually more viscous, and a thin skin forms upon its surface. With the "raw" oil this change takes place slowly, but with the "boiled" oil the reaction is more rapid, and a thin film of it will become quite solid in a short time; it is then said to have "dried."

The so-called drying of linseed oil is really not a drying process at all, because in all drying processes water or other liquid is evaporated, and this is not the case in the reaction above mentioned; nothing is evaporated, but, on the contrary, something is absorbed.

Sennebier and, later, De Saussure, found that oil absorbed oxygen, and Livache has estimated the increase in weight due to the absorption of oxygen when the oils were placed in contact with lead, which favours the reaction. The figures are as follow;—

Experiments on the Oxidation of Oils.
(Livache.)

	Increase in weight. After two days.		After seven days.
Linseed	14·3	..	—
Walnut	7·9	..	—
Poppy	6·8	..	—
Cotton-seed	5·9	..	—
Beech-nut	4·3	..	—
Colza	—	..	2·0
Sesame	—	..	2·4
Earth-nut	—	..	1·8
Rape	—	..	2·9
Olive	—	..	1·7

The experiments show that linseed oil has a much greater affinity for oxygen than any of the others, and the figures give the relative drying power of those oils that are capable of drying. Linseed oil consists almost entirely of the glycerides of linolic acid $(C_{18}H_{31}O_2)_3\ C_3H_5$, which is usually termed linolin, and of linolenic acid $(C_{18}H_{30}O_2)$. On decomposing linolin so as to obtain free linolic acid, this substance is found to be a yellow, oily fluid, similar to linseed oil in appearance. Immediately, however, it is brought into contact with air at a slightly elevated temperature, oxygen is rapidly absorbed, the acid turns brown, and quickly solidifies; it behaves in a similar manner to "boiled" oil, but the reaction is much more rapid.

Non-drying oils contain similar oily or fatty acids, but these have much less affinity for oxygen than linolic acid. Drying oils, therefore, derive their properties from the linolic acid which they contain. This acid has been discovered in several other drying oils that have been examined; no doubt it exists in all, their rate of drying being proportional to the amount of linolic acid present.

The non-drying oils contain, not linolic acid, but other acids which have less affinity for oxygen, and which therefore do not cause the oils to dry.

What is formed when an oil dries to a varnish-like mass is not yet known; the process is evidently, as shown, an oxidising one, and by the oxidation of linolic acid in other ways there is obtained a substance known as tetrahydroxy-stearic acid, $C_{18}H_{32}O_2\,(OH)_4$. The solid product from

linseed oil may contain this latter acid, or some similar substance, but this point has yet to be worked out. It appears to be a resinous body. The researches of Hazura prove that the acid in linseed is capable of being separated into two acids, linolic and linolenic.

When linseed oil is heated or "boiled" at a high temperature for several hours, irritating fumes are given off, containing acrolein, formic, and acetic acids, and a product known as "boiled" oil is produced. It has been shown that "boiled" oil dries much more rapidly than the "raw" oil, and the reason for this is not far to seek. It is known that when glycerine is heated, the above products, acrolein, etc., are evolved. As linseed oil contains the radical of glycerine, that is glyceryl C_3H_5 (glycerine being $C_3H_8O_3$), it is evident that during the boiling of oil the glyceryl, or glycerine radical, is decomposed in a similar manner to glycerine by the heat, consequently linolic acid is liberated, and remains dissolved in the oil. As pointed out, the acid has a very powerful affinity for oxygen, and this fact explains the reason why boiled oil is superior to the raw oil. It owes its superiority to the presence of free linolic acid.

Certain metallic compounds added to the oil during boiling increase the drying properties of the oil; compounds of linolic acid with the metals are formed, these compounds having a greater affinity for oxygen than even the free linolic acid

There are two methods in use for boiling linseed oil.

(1) The oil is heated to a high temperature over a naked flame until frothing occurs, when a lead or manganese compound is added, and the boiling continued. In this process water is first driven off; the mucilage is next destroyed by charring, and then the glycerine begins to be destroyed. The latter reaction is helped by the oxidising action of the metallic compounds added, the metals combining with the free linolic acid as fast as it is formed, so that the resulting boiled oil always contains either lead or manganese, whichever has been used. The process is somewhat dangerous, as the oil may easily take fire, and the finished product has always a more or less brown colour, supposed by many, though sometimes erroneously, to show a better quality than the paler oils.

(2) The oil is heated by steam, and during the process air is blown through it, either a lead or manganese compound being added at the same time. This process is, of course, without the danger that accrues from using an open fire, and the oil produced, not having been heated to such a high temperature, has a pale colour. The oxidation and destruction of the glycerine are chiefly performed by the air blown in.

Chevreul early demonstrated that manganese compounds were better than lead compounds as driers. He found that a boiled oil containing manganese absorbed oxygen so greedily from a limited volume of air as to leave nothing but nitrogen. The power of absorbing oxygen possessed by one hundred volumes of linseed oil compared with one hundred volumes of a mixture of linseed oil with a manganese oil was as 9·4 to 100. This may be termed its drying power. A mixture of linseed oil with about one-fourth of its volume of a manganese oil is a much better drier than either alone. This is a curious fact, but it shows that a limited amount of manganese is more beneficial than a large quantity. The reason for this is that a boiled oil containing much manganese dries hard very rapidly upon the surface, thus protecting the lower layers from oxidation, so that the mass remains tacky for an indefinite period.

Boiled oils may be prepared with other metals; their drying powers are as follows: Oil containing lead when spread in a thin layer dries in twenty-four hours; with manganese, five to six hours; with copper, zinc, and cobalt, thirty to thirty-six hours; with nickel, iron, chromium, etc., it requires more than forty-eight hours to dry.

Of course, if the oil is laid on more thickly it takes longer to dry, as the air cannot reach the under layers so quickly, and oxidation is therefore retarded. Hence thin layers of varnish are more efficient than thick ones. Partly for this reason, heat increases the drying power, because oil if heated may be laid on in a thinner coat; oxidation is also more rapid at a higher temperature.

Thus also when boiled oil is mixed with turpentine, a film of it may be laid on more thinly, and this dries more quickly than if the oil were used alone.

Turpentine acts simply by dilution, and evaporates away without acting as a drier. "Driers," or, as they are some-

times designated, "siccative" materials, are added to linseed oil or to paints in order to render them more quickly drying.

The driers generally used are metallic lead, litharge, a mixture of litharge and manganese sulphate, of lead and manganese nitrate, red-lead, lead acetate, lead linoleate, manganese borate, manganese oxide, manganese hydrate, manganese oxalate, manganese oleate, and manganese linoleate. Some of these, as has been shown, are added in the boiling process, others in mixing the paints. Paint mixed with boiled oil does not need special driers, but where a proportion of the raw oil is employed it may be benefited by adding the required metallic base so as to increase the affinity for oxygen.

The manganese driers are manganese dioxide (MnO_2); manganese borate; manganese sulphate ($MnSO_4$); manganese oleate; and manganese linoleate.

Litharge is the monoxide of lead (PbO); it is prepared by roasting lead in a reverberatory furnace, as in the first stage of the preparation of red-lead. The preparation of red- and white-lead has already been described.

Lead acetate is formed by dissolving metallic lead in acetic acid and crystallising out the compound.

Lead oleate is really a lead soap, known to the pharmaceutical chemist as "lead plaster"; it is formed by saponifying olive oil (olein) with caustic soda, and precipitating with a solution of lead acetate; the lead oleate separates as a yellow sticky mass which is washed and pressed.

Lead linoleate is prepared in an analogous manner to the oleate, using linseed oil in place of olive oil; it is a yellow mass, but in contact with air oxidises rapidly, turning brown; it is a very active drying agent, and is no doubt present in boiled oil prepared with litharge or red-lead.

Manganese dioxide (MnO_2) occurs native as the mineral pyrolusite; it is simply ground to a fine powder for use.

Manganese borate is formed by mixing together solutions of manganese sulphate and borax. Manganese sulphate is prepared by boiling manganese dioxide with sulphuric acid. The oleate and linoleate of manganese are prepared in a similar manner to the lead compounds, but using manganese sulphate for precipitating the soaps.

Ferrous sulphate or copperas ($FeSO_4$) is a useful drier owing to its property of decomposing to ferric oxide when oxidised, especially in the presence of moisture. It tends, however, to harden paint or varnish to cracking point, and so must be used carefully. It is inferior as a drier to the lead or manganese salts, and from 1 lb. to 2 lb. have to be added to every hundredweight of oil. The water of crystallisation must be driven off before use.

Zinc oxide (ZnO) is used to dilute driers, it having no drying properties. Zinc sulphate ($ZnSO_4$) is also used, but without advantage; to be of any use at all, the water of crystallisation contained in it must be dried off before it is incorporated with the paint oil. It is safer to leave out zinc sulphate.

The following is a method of preparing patent driers. Procure 20 lb. terra-alba or barytes, $\frac{1}{2}$ gal. boiled linseed oil, $\frac{1}{2}$ lb. acetate of lead, and $\frac{1}{4}$ lb. borate of manganese. Mix the barytes with half the boiled oil, and in another vessel dissolve the acetate of lead in $\frac{1}{4}$ pt. of boiling water, and mix with the barytes. The borate of manganese is then dissolved in $\frac{1}{4}$ pt. of cold water, and also added and well stirred; follow with the remainder of the boiled oil. The whole of the ingredients should next be thoroughly mixed into a uniform paste, when the preparation is ready for use in the proportion of 1 lb. of driers to 14 lb. of paint. Red-lead does not require the addition of driers, as it is a powerful drier when mixed with boiled oil.

Terebene, if carefully made, is a very powerful drier for paints, enamels, and varnishes. To prepare terebene, procure 28 lb. resin, 14 lb. powdered litharge, 14 lb. red-lead, 4 lb. slaked lime, 6 gal. clarified linseed oil, 18 gal. American turpentine, and 1 gal. boiled linseed oil. Melt the resin in a suitable vessel (copper preferred) over the fire and add the clarified oil, which should have been warmed. The temperature should now be raised by means of a moderate fire to 390° F., the mixture being stirred at intervals to prevent the oil boiling over the sides of the vessel. Then add the litharge and red-lead very slowly, sprinkling it in and constantly stirring until all is mixed. The slaked lime, followed by the boiled oil, may be added in a similar manner. The temperature is now raised to 460° F. and kept at this about an hour. A palette knife

should be dipped into the preparation at intervals, and if, on cooling, the substance deposited on the knife breaks hard and crisp, it is baked sufficient and should be allowed to cool down to about 240° F., and turps should be run, with constant stirring, into the preparation from a small tap fixed in the side of the vessel containing it. After about half the specified quantity of turps has been run in slowly, the remainder should be poured in quickly before the preparation has time to cool. The pan should next be placed on a very small fire and heated to 220° F. for about half an hour, the material being stirred well from the bottom of the pan. Do not exceed the temperature stated, as turpentine is highly inflammable. The mixture is next taken from the fire and placed in small tanks or cisterns to settle for about thirty days, when the clear portion is syphoned off and is then ready for use. If a darker and stronger terebene is required, 14 lb. of black oxide of manganese should be added with the red-lead and litharge.

In preparing gold size, first procure 50 lb. common kauri gum, 17½ gal. clarified linseed oil, 22 lb. red-lead, 18 lb. powdered litharge, 1 lb. borate of manganese, and 50 gal. American turpentine. Place the clarified oil in a copper pan, and with a steady fire heat the oil to a temperature of 400° F. In the gum-pan place the kauri gum, which should previously have been broken into pieces about the size of a walnut. Fuse the gum thoroughly, then take 4 gal. of the hot oil from the pan and pour it into the gum, which should be well stirred. The contents of the gum-pan should now be placed in the copper and the temperature raised slowly to 520° F., after which it should be allowed to cool down to 480° F. ; then add the litharge, lead, and borate, sprinkling them in very slowly. Keep the ingredients of the pan thoroughly well stirred whilst adding the driers, otherwise the pan would boil over and take fire with disastrous results. After the driers are added, allow to remain a few minutes, until a sample taken out on a knife and cooled in water breaks crisp between the fingers ; then let it cool to about 200° F. Add the turps exactly as in making the terebene above, and leave the gold-size in tanks to settle for about thirty days.

CHAPTER XIII.

PAINT GRINDING AND MIXING.

The usual method of grinding dry colours in oil is to place the pigments in a specially constructed mixer, and then mix them into a thick paste with raw linseed oil. They are then ground fine between granite rollers or flat stones driven by steam power. If the dry colours are in a finely divided state free from any grit, they may be mixed in oil and rubbed out on a slab by means of a palette knife until a uniform mixture is obtained. This mixture is then thinned down ready for use in the same way as are other paints.

A simple form of paint-grinding machine is the "cone" mill, which may be worked either by hand or by a belt from shafting. This machine consists in principle of two cones, one of which is fixed while the other revolves. The hopper is fixed by two binding screws, and may be removed for cleaning purposes. Against the bottom of the hopper is fitted a cone-shaped arrangement which is caused to revolve by spur wheels beneath; the mills are either made for working by hand (Fig. 42) or may be run from a shaft. The paint is placed in the hopper and falls by gravitation between the two conical surfaces, where it is ground into a uniform paste which oozes out at the junction and is scraped off from time to time, or it may be allowed to fall into a trough placed beneath for its collection.

Paint grinding is now very largely performed by roller mills, of which there are many forms; in this method it is necessary to mix the dry pigment and oil together in a pug mill before submitting it to the rolls.

The pug mill is sometimes worked alone, but very frequently it is fitted up as a part of the grinding machine, as in Fig. 43, which gives a section of a roller and pug mill combined. The pug mill consists of a cylindrical iron

vessel A (Fig. 43), having a shaft in the centre, attached to which are a series of arms or knives B; the shaft is caused to revolve, and the arms or knives then serve as beaters, thoroughly mixing and amalgamating any materials put into the mill. After agitation for a certain length of time, the mixture of oil and colour is allowed to flow from the opening at the bottom of the pug mill down a shoot, which delivers it between the first and

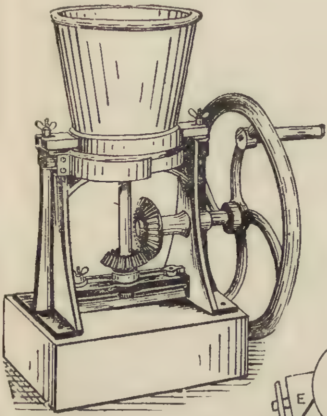


Fig. 42.—Hand-power Cone Mill.

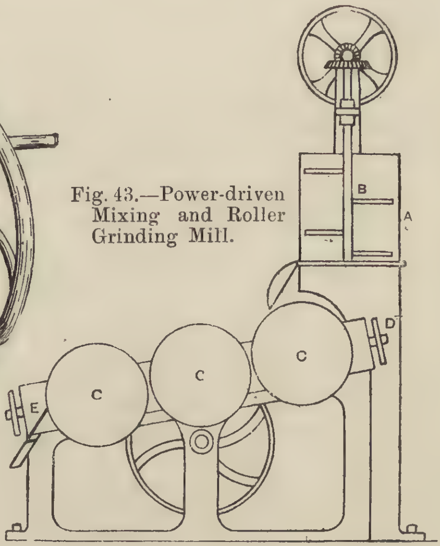


Fig. 43.—Power-driven Mixing and Roller Grinding Mill.

second rollers C; in these rollers the grinding begins, and the oil and colour are, so to speak, pressed closer in contact as they become more finely divided; the paint is then drawn over to the third roller by adhesion, is further ground, and is finally removed by the scraper E and falls down a shoot into the trolley or receptacle placed beneath to receive it.

The plant shown by Fig. 43 consists of two upright mixers or pug mills A (only one of which is shown in section), each fitted with a vertical shaft in the centre and with radiating arms; the shaft is caused to revolve by the

spur gearing and pulley shown above. The pug-wheels are worked in conjunction with a roller-grinding mill consisting of three large rollers C, made of granite, steel, or chilled iron, fitted in a heavy iron frame, bolted into a concrete foundation. The rollers are driven from the middle one by

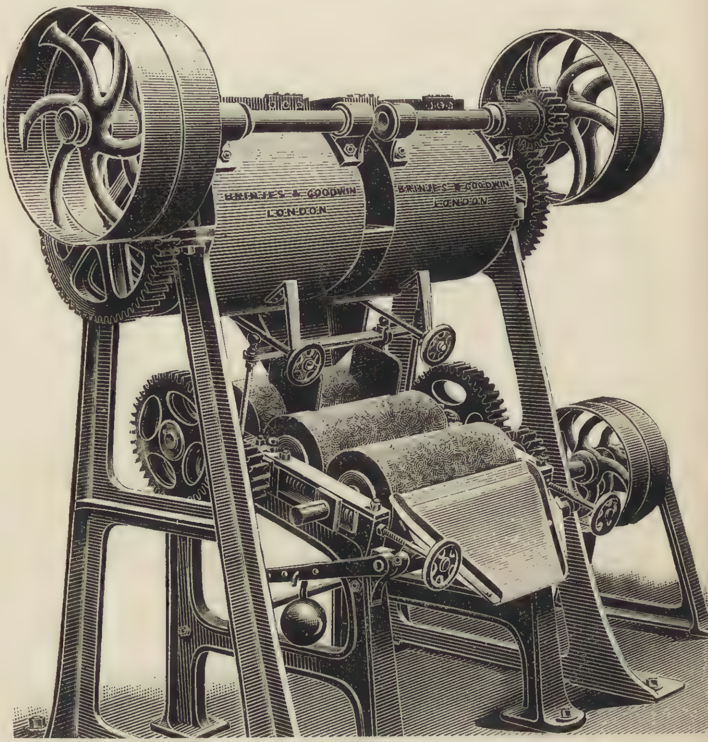


Fig. 44.—Triple Roller Mill with Two Pug Mills.

spur wheels, which are so arranged that the speeds of the rollers are different, the right-hand roller running much more slowly than that on the left, while the central one has a medium speed ; an arrangement is also fitted to some machines whereby the central roller has a lateral motion imparted to it with the object of submitting the material

passing through to a crushing as well as a grinding action; both the crushing and grinding actions are essential to the production of uniform paints. The rollers are brought in contact by the screws D. The machine is fitted with large fast and loose pulleys, and is driven by a belt. The excess of paint which might accumulate at the ends of the rollers and there fall off, is prevented from doing so by small scrapers set at such an angle that the paint is forced towards the centre of the rolls; the supply of paint from the pug mill is, of course, regulated so that there is no waste from over-charging.

Triple roller mills, in which the rollers are horizontal, are made by Hind, and by Followes and Bate. A combined pug mill and roller grinding machine is manufactured by Norris, and in this machine there are two pug mills, one of which is for mixing, while the other is for delivering the mixed paint to the rolls. Fig. 44 shows a combined mill made by Brinjes and Goodwin, who have kindly lent the block.

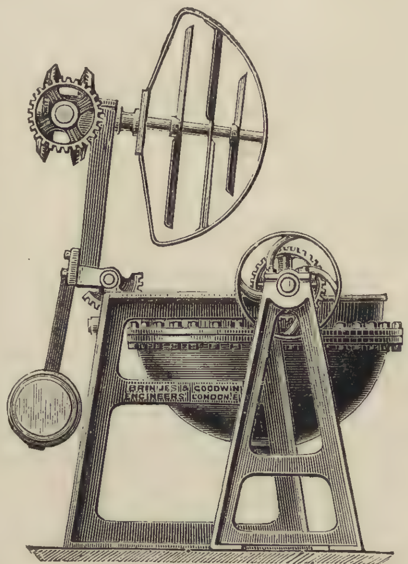


Fig. 45.—Paint Mixer.

For extremely fine grinding, two sets of triple rollers are sometimes employed. The paint as it leaves the rollers is a uniform semi-solid mass, having a creamy consistency; it is either sent out in this state—that is, simply "ground in oil"—or it is further mixed with the necessary quantity of oils, driers, and turpentine, for sale as a "ready mixed" paint.

In grinding the different pigments varying proportions of oil are employed by different manufacturers; and it will

need but little demonstration to prove that heavy pigments, such as white-lead, require less oil to reduce them to the condition of paste than does, for instance, lampblack, which, for an equal weight, has many times the bulk of lead. As may be seen from the following table, given by Professor Church in his handbook on the "Chemistry of Paints," the variation is very great:—

	Amount of Oil in lbs. Required to Grind 100 lbs. of Pigment.	
	According to Pettenkofer.	*According to Winsor and Newton.*
White-lead	12	15
Zinc white	14	—
Aureolin..	—	200
Chrome yellow	19	32
Yellow ochre	75	75
Raw sienna	240	180
Vermilion	25	20
Madder lake	62	125
Terre verte	100	70
Viridian	—	75
Prussian blue	112	75
Cobalt blue	125	75
Ultramarine (artificial)	—	37
Raw umber	—	100
Burnt umber	—	90
Bitumen	—	126
Brown madder	—	87
Burnt sienna	181	195
Bone black	112	110

In the manufacture of ready-mixed paints, the pigment already ground in oil is mixed with the requisite quantity of oil and turpentine, either in a pug mill, like Fig. 43, or in some special form of mixer. Fig. 45 shows a mixer made by Brinjes and Goodwin, the mixing apparatus consisting of a frame and knives revolving in the one direction, while the central spindle with its attached knives revolves in the opposite direction. A horizontal mixer is made by Followes and Bate; it has four L-shaped beaters attached to the central spindle in such a way that the paint in every part of the apparatus is efficiently mixed.

The mixers made by Werner, Pfleiderer and Perkins, Ltd. (Fig. 46), have a U-shaped vessel, in which revolve two blades of a peculiar zig-zag form, and so constructed that they revolve in opposite directions, sweeping extremely close to each other and to the bottom of the pan, so that almost

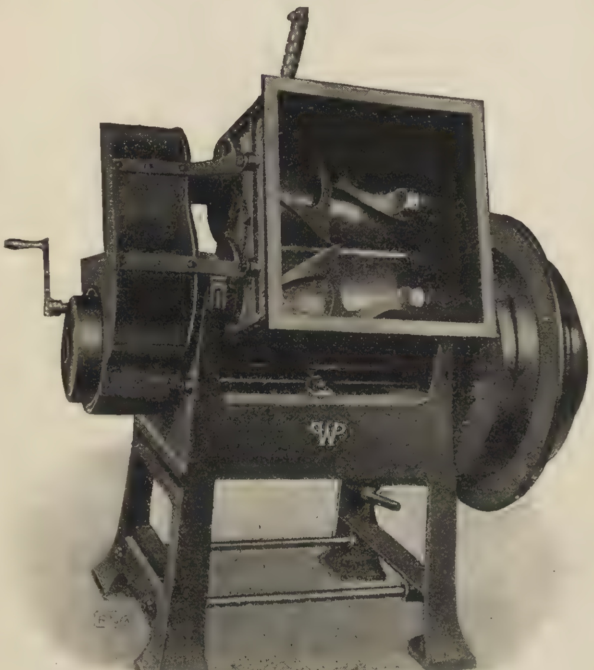


Fig. 46.—Universal Mixing Machine.

every particle of the paint is kept in motion. These mixers are fitted with reversing gear, and with a screw or winch for tilting the pan when the material has to be emptied out. There are also several forms of mixing machines in which the revolving blades are placed vertically.

CHAPTER XIV.

GUMS, OILS, AND SOLVENTS FOR VARNISHES.

Although the art of varnish making was known to the ancients, it was only during the last century that the manufacture was brought to anything like perfection. The proficiency of the ancients was, however, by no means despicable, as the varnish-coated articles found in the ruins of Pompeii and Herculaneum can testify. The Chinese, and also the inhabitants of the East Indies, have practised the art of varnish making from time immemorial.

By varnish is understood, an authority has said, any liquid substance whose diffusion over solid bodies gives to their surface a certain brilliancy, by the combined effects of reflection and refraction of the rays of light. Commonly, the term varnish is applied to any material which gives a permanent lustre to a surface. Drying oil thickened by the action of the sun or by boiling, for instance, has been used as a varnish, but in speaking of varnish reference is usually made to a solution of gum or gums—resinous, fossil or semi-fossil—and boiled oil with an essential oil added to the gum to make it more fluid.

In varnish manufacture, the selected gums are boiled in a fixed oil (linseed oil) to which an essential oil (turpentine) is added to prevent its being viscid. The essential oil being of the nature of a spirit causes the varnish to flow, but it quickly evaporates, with the result that the varnish sets rapidly; once set, the varnish must not be touched till dry. Although it sets in five minutes, it does not dry in less than twelve hours.

The many gums or resins used in varnish making are all exudations from various species of trees, some of which have disappeared centuries ago, leaving the resins embedded in the soil and covered with decayed vegetation. This is sought for by the natives of the different countries, who clean it and dispose of it to traders for a trifling sum.

The qualities of the resins depend much upon the durability, transparency, solubility, lustre, and specific gravity.

The gums or resins include animi, copal, amber, kauri, sandarac, resin, mastic, dammar, shellac, benzoin, etc. These are known in the trade generally as gums, though it is usual now to apply this term to those only that are soluble in water, such as gum arabic, etc., and to class all those insoluble in water—copal, for instance—as resins.

The resins and gums have certain characteristics in common; they occur usually in rounded masses, nodules, or tears; a few appear in flattened masses or in thin plates; they are generally hard, brittle, and transparent, and either colourless or white, yellow, or brown. They are all a little heavier than water, the specific gravities of the different resins varying between 1·01 and 1·24. Of the chemical composition of these products but little is known; they all contain carbon, hydrogen, and oxygen, and they behave generally as weak acids. The resins and gums are somewhat differently affected by solvents, and for the present purpose they may be conveniently placed in three classes, as follows:—

1. Resins used in the manufacture of oil varnishes.
2. Resins employed for spirit varnishes.
3. True gums, soluble or softened by water.

The resins of the first group are very hard and difficult to dissolve, and, though it has been found possible to bring them into solution by heating with turpentine under pressure, they are usually fused by heat and incorporated with boiling linseed oil.

The resins of the second group, though brittle, are somewhat softer, and are more easily dissolved by either alcohol or turpentine.

The gums of the third group either dissolve easily in water or form with it a thick mucilage.

Colophony or resin is the residue left in the stills after the distillation of turpentine. It is contained in the state of solution in the natural turpentine or gum thus derived from several species of pines, and is simply separated as a by-product in the manufacture of the volatile oil or spirit of turpentine. Resin is usually imported in barrels into which it was poured in the melted condition; it is

therefore usually in very large masses, which, if of good quality, are pale amber coloured and quite transparent, but the common kinds are dark-brown or nearly black. Resin is an oxidation product of turpentine, and it is a well-known fact that oil of turpentine on keeping gradually thickens or becomes fatty, and will further solidify after a time; this change is brought about by the absorption of oxygen and the formation of resin. Resin is much more brittle than the other oil-varnish resins, and is easily melted; it is readily soluble in turpentine, alcohol, etc. Used alone, it forms very brittle varnishes, and it is principally used for the cheaper class of goods, such as common oil varnishes, cheap spirit varnishes, and naphtha varnishes. By itself it leaves rather a hard, brittle, and lustrous coat, but, tempered with some oil or soft resin, it makes a durable varnish, not, of course, approaching the copals or kauri in this quality.

Glass resin is an exudation of the pine *Pinus australis*, which is a native of the United States. It is prepared by distilling the palest and cleanest gum-thus, which is the commercial name for the crude resin, whilst the dark resin is made from the ordinary gum-thus. It is insoluble in water, but is soluble in alcohol, benzine, naphtha, ether, and turpentine. It is much used in cheap varnish making in combination with the kauri and copal, and in the manufacture of ships' white composition. It melts at 200° F., and its specific gravity is 1·06.

Copal is a name originally applied to all fossil gums derived from tropical Africa, from Sierra Leone, South America, and Manila. They are procured in a great variety of colours. The dammar gums from Java, Singapore, and Penang, are used for spirit and turpentine varnishes on account of the absence of colouring matter. Copal is the resin most largely used in varnish making, and there are several varieties of it.

Sierra Leone copal is, as its name implies, obtained from Sierra Leone, as also from adjacent parts of Africa; it occurs in the fossil state in the subsoil, and it is said to be also produced by the tree *Copaifera Guibourtiana*. It is found in irregular pieces or nodules of a pale yellow colour, and is quite transparent; it is an excellent varnish resin, and is difficult to fuse. The material is very hard and

transparent, and is slightly soluble in turpentine; to make it soluble, it is usually fused or run over a fire by means of a specially constructed copper pan. It is used in manufacturing all kinds of hard varnishes, as church, carriage, and oak varnishes. It melts at 420° F., and has a specific gravity of 1·063.

Zanzibar copal or animi, of which there are two varieties, "recent" and "fossil," is the product of a tree, *Trachylobium Hornemannianum*, growing in Zanzibar and parts of Africa, and brought by the natives to Zanzibar, whence it is shipped. The fossil animi is found in the reddish subsoil in and around Zanzibar, and is superior to the recent, being of greater hardness. Animi comes into commerce in irregular or tabular pieces of a pale yellow or yellowish-brown colour, and has a peculiar roughened surface called "goose skin"; it is vitreous and transparent. Animi is a very hard resin, and for varnish-making purposes it ranks next to amber; owing to the difficulty experienced in melting it the varnishes made from it are rather dark coloured, but they are very durable. Animi melts at 470° F., and is slightly soluble in ether, chloroform, benzine, and turpentine. Its specific gravity is 1·06.

Pebble copal comes from Sierra Leone, and is another product of *Copaifera Guibourtiana* or some similar tree. It occurs in the form of nodules, with a roughened surface, in the beds of, or near to, rivers, down which it has evidently been carried.

Angola, Loango, and Gaboon copals are other varieties coming from parts of Africa, and though they resemble those previously mentioned, they are not so good; they vary from a pale yellow to a reddish colour, and have other points of difference. Angola copal is obtained not only from Angola, but also from the Congo and other neighbouring parts. The sources of Gaboon copal and Loango copal are indicated by their names.

West Indian copal is obtained from Brazil and other countries in South America; it is sometimes found in the fossil state, but it is also derived from the tree *Hymenæa Courbaril*. This resin occurs in irregular masses, is transparent, and of a pale yellow colour; it is an excellent varnish resin, but somewhat softer than the best copal.

Kauri may be distinguished from the true copals by its greater brittleness, and by its rather resinous odour when fractured; it is also easily softened by alcohol and is quite soluble in ether, whereas the copals are but slightly affected by these solvents. Kauri ("cowdee, kowrie, or cawree gum") is obtained from several species of pines growing in New Zealand, but mostly from the kauri pine (*Dammara australis*). Kauri is found very extensively in the fossil condition, simply embedded in the soil just below the surface, and "recent" kauri is obtained by tapping the trees, from which a juice exudes which very soon solidifies. Kauri occurs in lumps of various sizes; it is usually transparent, but sometimes cloudy or opaque; in colour it is pale yellow or brown, and when broken it exudes a peculiar resinous odour. Kauri is rather softer than the copals, and yields a varnish which is not so hard or so durable as the latter; nevertheless the kauri resin is now very largely used. As already stated, kauri is entirely soluble in ether, and is slightly soluble in alcohol, benzol, and turpentine. After melting or fusing, it is soluble in petroleum, ether, oils, and turpentine. It is chiefly used in the manufacture of oak varnishes. It melts at 350° F., and its specific gravity is 1·05.

Recent kauri—the resin obtained from living trees—has been claimed to be assimilated with oil more readily than any other gum. Less heat being necessary, there is less danger of the varnish browning, and thus a paler varnish is produced. It is more permanent than mastic, does not crack, but will not, as mastic does, make megilp.

Amber (known in mineralogy as succinite) is the mineralised or fossil resin of an extinct pine tree (probably *Pinites succinifer*), and is found in strata of the Cretaceous period in Germany, Russia, and in North America, a very small quantity having been found also in Great Britain; it is frequently thrown up by the sea on the east coast of England, but not in any quantity, and in Prussia regular mining is carried on for the raising of this resin. It occurs in beds of lignite and in alluvial soils, but it is found in greatest abundance on the shores of the Baltic, between Königsberg and Memel; its form may be round, irregular lumps, grains, or drops. It is hard, rather brittle, and has a perfectly conchoidal fracture, that is,

the surface of the fracture has convex elevations and concave depressions. In colour it ranges from almost colourless to very dark brown or reddish-brown; it may be transparent, translucent, or opaque. The finest kinds of resin are cut for jewellery or decorative purposes, only the commoner dark-coloured sorts or small pieces being available for varnish making.

Owing to the scarcity of amber it commands a high price, and therefore its use is limited, but it forms one of the finest and hardest varnishes. It is insoluble in acetic acid, ammonia, water, benzine, carbon bisulphide, alcohol, chloroform, and slightly soluble in ether and turpentine, and melts at 550° F., when it is soluble in mineral naphthas, turpentine, and petroleum.

A curious property of amber, but one of no interest to the painter, is that it becomes negatively electric by friction, and the power of electrified amber to attract light bodies was known as early as 600 B.C. Its specific gravity varies from 1·05 to 1·07, sometimes reaching 1·1. It is without taste or smell, but when heated by friction or otherwise it emits an agreeable odour; it burns with a clear flame and a pleasant smell, leaving about 1 per cent. of ash. Analysis shows that it contains from 3 to 8 per cent. of succinic acid; there are two resins present, one melting at 295° F. and soluble in ether, but not in alcohol; and another resin melting at 221° F. and soluble in alcohol and other bodies. When its soluble constituents have been dissolved out by means of ether, amber has a similar composition to camphor—$C_{10}H_{16}O$. On distillation, amber yields an empyreumatic oil which is a mixture of hydrocarbons and succinic acid.

Sometimes amber encloses crustacea, centipedes, and insects belonging to species which do not exist now; amber has been found enclosing leaves. The most valuable amber is of an opaque lemon colour, and is known as fat amber.

Amber may be distinguished from fossil copal by heating a particle and holding a piece of moistened lead acetate test paper in the fumes. If it is amber, the paper will be blackened; if copal, the paper will not be discoloured.

Asphaltum, or native bitumen, is used in the manufac-

ture of black varnishes and japans. It occurs naturally in Albania, South America, Barbadoes, and in the great lake of Trinidad. It resembles pitch in appearance, and is insoluble in water and àlcohol, but dissolves readily in turpentine and in the naphthas. It is much used by varnish manufacturers for making black varnish, black japans and brunswick blacks, and its specific gravity is 1·06. Cheap black varnishes are made by mixing various kinds of pitch obtained in the distillation of oily products of animal or vegetable origin. Although included here for the sake of convenience, neither asphaltum nor pitch is a member of the resin group.

This concludes the description of the resins used chiefly in the manufacture of oil varnish. Those about to be described are mostly used in spirit varnishes, although one or two enter at times into the composition of oil varnishes as well.

Lac occurs in commerce in several forms; stick lac consists of twigs enveloped with the lac, but this form is not used; seed lac consists of small grains; shellac occurs in thin orange-coloured leaves, more or less agglomerated; button lac is a darker kind occurring in irregular disc-shaped pieces; garnet lac occurs in thick plates of a dark red colour; and there is also white or bleached shellac.

Lac is a misnomer, since the term may embrace other products, as seed lac, lump lac, stick lac, cake lac, garnet, button, liver, and the better known shell lac (shellac), designations that refer chiefly to the form of the gum known in commerce. Lac is a resinous incrustation surrounding the twigs or extreme branches of trees (chiefly dhak trees, *Butea frondosa*), which abound in Bengal and Assam, also in smaller quantities in the Punjaub, Bombay, Madras, Burmah, Siam, Ceylon, and some parts of China. Siamese lac is by some authorities regarded as the best kind of lac. The quantities produced and utilised vary greatly in different provinces. Some forests simply abound in lac, which, however, is not utilised to the full extent owing to scarcity of labour and cost of transport, whilst that of inferior quality may be readily accessible.

It is believed to be an exudation from the bark following punctures made by an insect known as *Coccus lacca*, whilst by others it is asserted to be an exudation from

the bodies of the insects which abound in great quantities near the junction of the smaller twigs, and are often even embedded in the secretions. There are usually two gatherings—the first in March, the second in October; the gatherings vary much in quantity and quality, the brightest being generally considered the best consistent with its bulk, the incrustation sometimes being ½ in. thick around the twigs. For commercial and propagation purposes the twigs are cut off, one portion being placed over and secured to the branches of fresh trees, the other being cut up into lengths of 3 in. or 4 in., in which form it is passed on to the manufacturers of shellac in its various forms. Practically, the bulk of it is treated within easy reach of the forests; possibly there may be but one English firm which imports and deals with it in its crude state.

The first part of the process is to separate the lac from the twigs by passing between rollers, then winnowing, and afterwards sorting and picking by native women. The crude lac is then placed in long canvas bags of fine texture; this in turn is held over charcoal fires, a woman at each end twisting and twirling the bag around till the lac becomes molten and oozes through the canvas. Alongside the fire is fixed a stout bamboo pole about 4 in. in diameter and 3 to 4 ft. long; the interior of this pole is filled with hot sand. A third woman take up a portion of the liquid lac by means of an aloe leaf or plantain bark. The bamboo is touched here and there, and by a deft turn of the wrist the lac is spread around till a film of it nearly covers the pole. The lac dries rapidly and is broken up into many pieces; in this form it passes into the polisher's hands as shellac, except that it reaches him very much broken up, owing to the endeavour of the exporter to get as much as possible in the smallest space. Shellac varies from a pale orange colour to a very dark garnet red; it is transparent in thin films and very brittle.

Sheet lac is made in a similar manner, except that it is removed from the bamboo whilst still supple and stretched over the fire in order to remove the wavy appearance peculiar to shellac.

By another method of preparing crude lac, the twigs containing the lac are collected from the trees and are beaten with a mallet, which dislodges the lac, which is

then placed in a large vat along with water while the natives knead it about with their feet until most of the colouring matter, or lac dye (see p. 86), is removed. The lac is next placed in a coarse cloth bag, which is held at each end by two natives while it is exposed to the heat of a fire; below the bag is a small trough into which the melted lac from the bag collects. A third native ladles out the melted lac and pours it over a roller covered with brass, which is caused to revolve and thereby forms the lac into thin sheets; this is the shellac.

Button lac is generally much darker in colour, and is made by dropping instead of spreading. In form it resembles large buttons, whence its name.

Garnet or liver lac is another form of the dark variety.

Seed lac resembling small seeds is rarely used except for high-grade varnishes; it is more extensively used by lacquer makers. By some it is considered a purer lac owing to the absence of heat in its preparation, it being the lac as first obtained by grinding and winnowing from the twigs.

The process of extracting lac is much simplified by the use of modern machinery and the substitution of steam chests for charcoal fires. The modern methods, however, have certain disadvantages; the crude lac goes through one or more washings in water strongly impregnated with lime, and it is heated to a higher degree and often treated with resin to act as a flux and prevent the lac adhering to the sides of the vessels in which it is being treated; and these methods of treatment account in no small measure for a fault experienced polishers often meet with —namely, a sticky or gummy feeling when using some brands of lac.

White lac, better known as bleached lac, may be made from any of the common lacs, about 10 lb. of lac being slowly dissolved in 10 gal. of boiling water in which has been dissolved 3 lb. of common washing soda. The shellac is added slowly, each portion being allowed to dissolve before more is added. When all is dissolved, boiling continues for a few minutes longer, then the vessel is closed with a tight-fitting wooden lid, which is luted on with clay. When cold, a fatty substance is skimmed off the top, and the liquid is strained. The lac is then pre-

cipitated with dilute sulphuric acid added drop by drop; the mass is then washed to remove the acid, after which it is softened again by placing in boiling water; while in this plastic state it is well worked about and afterwards pulled by the hands into the long twisted rods with a silver-white brilliant surface so familiar to experienced polishers who make their own polish. It should be stored away in water containing glycerine. When required for use, it should be finely crushed, then spread out on clean paper in order to dry out any moisture before dissolving in spirits. It improves with age, if kept tightly corked in stone jars.

Another method of preparing white lac is to dissolve shellac in a solution of carbonate of potash, adding eau de Javelle (hypochlorite of potash) and hydrochloric acid; the shellac is immediately precipitated as a white flocculent mass; it is washed, dried, melted, and, while plastic, rolled into sticks.

Lac is soluble in alcohol and ether, and partially soluble in turpentine. Its specific gravity is 1·12. It is much used in white polishes, knottings, and all spirit varnishes. For instance, by dissolving 2 lb. of shellac in 1 gal. of methylated spirit, it may be used as a varnish for inside work, also as a shellac knotting. It is also made into French polish by dissolving together shellac 2 lb., gum benzoin 4 oz., and methylated spirit 1 gal., shaking at intervals until dissolved. It is also employed in the preparation of brown hard and white hard spirit varnishes and furniture varnishes by dissolving in methylated spirit, and adding Bismarck brown, red sanders wood, oak stain, or any aniline dyes soluble in spirits.

Other spirit varnish gums may now be considered.

Of the several varieties of dammar, Singapore, or white, dammar is an exudation from the Amboyna pine (*Dammara orientalis*), a large tree growing in Malacca, Java, Sumatra, and Borneo, the supply being chiefly imported *viâ* Singapore. Singapore dammar usually appears in colourless or pale yellow nodules, transparent and very friable; it is easily melted and readily dissolved by turpentine. Rock dammar, which is similar, and equal in quality, to the foregoing, is obtained from the *Hopea odorata* (Burma) and *Hopea micrantha* (Malay States). The resin from the

former tree is pale and sometimes colourless; that of the latter is darker and rather harder. Sal dammar is the product of the sal tree (*Shorea robusta*), which is found along the Himalayas, in West Bengal, Borneo, Sumatra, and the Malaccas; it is principally used for paper varnishes and in the manufacture of tracing paper, it being in the form of cream-coloured opaque pieces. Black dammar is the product of the *Canarium strictum*, of Tinnevelli, and occurs in irregular pieces of a black or dark brown colour.

Dammar is soluble in turpentine, oil, ether, and benzol. It is much used in the preparation of white paper varnishes. Its melting point is 240° F., and its specific gravity is 1·07.

Gum sandarach is of the juniper variety; it is a very soft, bright gum that easily scratches—an exudation of *Callitris quadrivalvis*, a tree indigenous to the mountains of North Africa. In the form of juniper berries, which closely resemble currants, it was formerly used as a medicine. It is collected by the Moors, and chiefly exported to Europe from Mogador. The resin, which closely resembles tears or pears in shape, and is semi-transparent, is the only portion used for varnish making. But, as already indicated, it is very soft; consequently, it is usual to add other gums—gum arabic if required for glaze, shellac if required for spirit varnish.

Sandarach is similar to glass resin in colour, and is entirely soluble in alcohol, and slightly soluble in benzine, petroleum, and turpentine. It is not used in oil varnishes, as it will not stand exposure to the weather. It is much used in making white hard spirit varnish. It melts at 320° F., and its specific gravity is 1·05.

Gum benzoin, or gum benjamin, is obtained from the tree *Styrax benzoin*, growing in India, Siam, and the Malay Archipelago. It is a peculiar looking resin, occurring in very large blocks, the ground mass of a grey or brownish colour indented with amygdules or almond-shaped particles of a cream colour. It has been likened in appearance to pieces of broken marble. It is a soft resin, but rather brittle, and easily pulverised even between the fingers; it has a pleasant fragrant odour. Benzoin is used only for glazing purposes, or for imparting a gloss to varnishes, but the film it forms has no durability. It is entirely

soluble in alcohol, and slightly soluble in ether and turpentine, has a fragrant odour, and is much used in spirit varnishes and making perfumes. Its specific gravity is 1·06. Benzoïn improves with age.

Manila copal is the useful product of a tree which grows in the Philippine Islands. This substance is not a true copal, being much softer and more easily fused than the copals, and it is in the form of nodules of a yellow or brown colour. It much resembles the common species of kauri gums in appearance. It is soluble in ether, absolute alcohol, and slightly soluble in benzine, chloroform, turpentine, and petroleum. It is much used to give elasticity to spirit varnishes, generally in combination with sandarach. It is also used in making enamels and compositions. It melts at 240° F., and its specific gravity is 1·07.

Elemi is used for softening varnish films or for counteracting the effect of brittle resins when they are also present. There is some confusion as to the sources of its chief varieties, but the following statement probably sums up the truth. Manila elemi is produced by the *Canarium commune*, which grows principally in the island of Luyon, in the Philippines, its distinctive name being due to the port through which come all the supplies. When pure and of good quality this is white, other kinds being grey or mixtures. The soft resin has a granular appearance, and on exposure to the air the volatile oil evaporates and the elemi hardens. On distillation, elemi yields about 10 per cent. of an oil having a similar composition to turpentine. Elemi is soluble in alcohol, etc., and produces a soft but brilliant varnish.

Mexican or Vera Cruz elemi, the product of *Amyris elemifera*, has most of the properties of the Manila variety, but is darker and harder, and less quantities of it are available. Species of *Bursera* also yield this variety, it is believed. Brazilian elemi, obtained from species of *Protium* (*Icica*), is of no importance to the painter. Mauritius elemi, coming from *Colophonia Mauritiana* or from *Canarium paniculatum*, has much the appearance and properties of Manila copal, but is without its importance.

Mastic is obtained principally from Scio, in the Grecian Archipelago, and is an exudation—obtained by incision—

from the shrub *Pistacia lentiscus.* It is collected by making incisions in the bark of the plant, from which the resin exudes. Mastic occurs in the form of small spherules or tears of a pale yellow colour and opaque It is extremely brittle and easily melted, but forms very glossy varnishes, which are, however, not durable. It is entirely soluble in alcohol and turpentine, and is insoluble in petroleum spirit. It is used in preparing the well-known mastic varnish for pictures. It melts at 230° F., and its specific gravity is 1·058.

Dragon's blood is a name given to many substances of different characters; but the only one of these possessing importance is the resinous exudation upon the nearly mature fruit of the *Calamus draco*, a ratan-palm growing in the Malay Archipelago and in other parts of Eastern Asia. The fruit of the tree is shaken into baskets, and the friable resin is then sifted from the stems and débris. It is softened by the sun or in boiling water, and is cast into rolls by wrapping it in palm leaves, in which form it reaches the European market. Generally, the round sticks are about 13 in. or 14 in. long and nearly 1 in. thick, and the resin has a blackish-brown colour. When cut up into thin slices it is found to be transparent, and to have the colour of deep crimson. Its specific gravity is about 1·2, the higher the better. It melts at about 120° C., and is soluble in alcohol, benzol, chloroform, carbon bisulphide, petroleum spirit, alkalis, etc., but it is only slightly soluble in ether, and it is insoluble in turpentine. Its chief use is to stain spirit varnishes and polishes to a fine red or mahogany colour. A few varieties of dragon's blood obtained from trees other than *Calamus draco* are not available in commercial quantities. The gums more or less soluble in water will now be mentioned.

Gum arabic is a product derived from several species of *Acacia* growing in parts of Africa, India, and Australia. It occurs in small rounded nodules, or in pipe-like pieces, sometimes colourless, but usually pale yellow to brownish yellow in colour; it is very brittle, and usually transparent. Gum arabic dissolves readily in cold water, forming a viscous liquid; it is insoluble in spirit, and is precipitated from solution in water if spirit be added. Gum-arabic solution is used as a glaze and medium for

ticket writing. An inferior gum, known as "gum ghatti," comes from India.

Gum tragacanth or gum dragon is the product of certain species of *Astragalus* growing in Palestine and Turkey-in-Asia. It occurs in peculiar leaf- or moss-like pieces of milky-white or greyish-white colour; it is opaque, hard, and tough. Treated with water it swells up, forming a very thick emulsion or mucilage, but this cannot be described as a solution. The liquid is sometimes used as a substitute for gum arabic.

The solvents largely used in varnish making are:—1, Boiled linseed oil; 2, turpentine; 3, methylated spirit; 4, wood naphtha; 5, ether; 6, coal-tar naphtha; 7, water. Amyl alcohol, acetone, and other solvents are also coming into use.

In the preparation of all oil varnishes, linseed oil may be looked upon as the solvent; the oil for this purpose is boiled, and it is incorporated with the gum reduced to a fluid condition by melting; afterwards the varnish is thinned with turpentine. Turpentine is used as a diluent in the oil varnishes, and in some of the spirit varnishes it is employed as a solvent.

The source, preparation and properties of linseed oil are gone into fully in Chapter I., and some special information with regard to the production of varnish-makers' pale-drying oils may now be presented.

In the production of a pale-drying oil for use in making varnishes, it is usual either to heat with steam or to add a certain quantity of water to linseed oil and allow a portion only to boil off, so that the temperature does not rise above 212° F. If protoxide of manganese cannot be obtained, as a substitute add sulphate of manganese and caustic soda (forming protoxide of manganese), or sulphate of manganese and carbonate of soda (forming carbonate of manganese), the last being the cheapest. Try these on an experimental scale. Take 18 parts of water, and add $2\frac{3}{4}$ parts of dry caustic soda or $3\frac{1}{2}$ parts of carbonate of soda. Take another 18 parts of water and dissolve in it $4\frac{1}{2}$ parts of manganese sulphate (protosulphate); measure out 100 parts of oil. All being now ready, pour the manganese sulphate into the boiler, then add the soda; stir well, and immediately after pour in the linseed oil. There

will then be a lower layer of water containing manganese protoxide or manganese carbonate in suspension, and the upper layer of oil, which will prevent the manganese compound oxidising. Now heat gently, and stir for the requisite length of time, cover up, allow to settle, and syphon off the clear oil.

Linseed oil may be prepared as a pale-drying oil by first refining it or treating it with a 5-per-cent. solution of potash, 30° Beaumé, or a 3-per-cent. solution of sulphuric acid mixed with the same bulk of water. The oil is then agitated for some time and left to rest, when the acid or alkali will settle at the bottom. It is then run off and the oil is well washed, steam and water being blown into it until all traces of the acid have disappeared. The water when settled is run off, leaving the oil ready for use. The alkali or acid decomposes the suspended mucilaginous matter, which is afterwards washed out by the steam and water, thus rendering the oil somewhat paler, purer, and less liable to turn rancid.

Another process is to procure the palest raw linseed oil direct from the mills and place it over a steady fire, continually stirring until a temperature of 520° F. is reached. It is then taken from the fire and allowed to stand about twenty-four hours, when the clear oil is ladled off; do not disturb the bottom of the oil, which resembles sago in appearance, this being the mucilage which has previously been suspended. The oil thus prepared is known as clarified oil, and is much used for preparing pale varnishes, being much less liable to ignite than the oils containing mucilage and moisture. To add drying properties to these oils heat 100 gal. by means of a steam coil to 210° F. In another vessel place 6 gal. of the oil, heat to about 360° F., then, while continually stirring, add 14 lb. of lead acetate steadily, as it causes effervescence and may boil over and ignite. Then add 17 lb. of white sulphate of manganese, which has been previously mixed in $\frac{1}{2}$ gal. of water, using the same precautions as with the lead acetate. The oil should next be boiled until all traces of the water have disappeared, when it is poured steadily into the tank containing the oil, which is agitated by having steam blown into it for about half an hour; this causes it to absorb oxygen rapidly. It is then allowed to cool down,

when it is placed in tanks for several weeks till ready for use.

The drying oil prepared by this process is exceedingly pale in colour, this being due to the colourless driers employed in its preparation. It may be used in manufacturing all pale oil varnishes as oil paper varnish, maple, copal, carriage, body, dial, and pale oak varnishes, and may also be used for mixing with all delicate colours without altering their tone or brilliancy; finally it dries perfectly hard in a few hours without losing its elasticity.

When boiled linseed oil is mixed with mastic varnish the mixture becomes a jelly; and in that state is the megilp so much used by artists.

Turpentine dissolves resin or colophony, dammar and mastic; it slightly dissolves the copals, kauri, amber, lac (shellac, etc.), sandarach, benzoin and manila copal. *Alcohol* (used in the form of methylated spirit) dissolves amber, lac, sandarach, benzoin, manila copal, elemi, mastic, and dragon's blood; it slightly dissolves kauri and some other resins. *Ether* dissolves kauri and manila copal; it slightly dissolves benzoin, dragon's blood, and amber. *Coal-tar naphtha or benzene* dissolves dammar and dragon's blood; it slightly dissolves kauri; it is known also as benzol, and is constantly confused with petroleum spirit or petroleum ether, to which the terms "benzine" and "benzoline" are wrongly applied. *Benzine or petroleum spirit* dissolves amber and dragon's blood; it slightly dissolves sandarach and manila copal. *Acetic acid* dissolves amber. *Ammonia* dissolves amber and dragon's blood. *Carbon bisulphide* dissolves amber and dragon's blood. *Chloroform* dissolves amber and dragon's blood; it slightly dissolves manila copal. *Water* dissolves gum arabic; it slightly dissolves gum tragacanth.

Turpentine for making varnish should be pure, strong, and free from acid. The longer it is kept before using for this purpose, the better it is. Its source, collection, preparation and properties are fully treated in Chapter I.

Methylated spirit is the solvent usually employed in the spirit varnishes; notable examples are French polish and shellac varnish, which are solutions of shellac in spirit.

Methylated spirit is impure alcohol, and alcohol itself is one member of a large series of organic products known

by the generic term of alcohols. The lowest member of this series is methyl alcohol, which is contained in wood spirit; the next is ethyl alcohol, which is the ordinary alcohol; higher still are propyl alcohol and amyl alcohol, contained in fusel oil. There are also several others.

Ordinary or ethyl alcohol is formed by the fermentation of sugar by means of yeast. There are two stages in the fermentation; in the first place, cane sugar takes up water and becomes "invert" sugar. This is then decomposed, yielding alcohol, carbonic acid, and minor products.

Starch in the form of potato starch, rice, barley, and Indian corn is also used in the preparation of alcohol, but it has first to be converted into sugar. This is done either with malt or with sulphuric acid. The alcohol produced is extremely weak; it is then distilled carefully, and leaves most of the water and all the solid matter in the still. Another distillation produces rectified spirit containing 84 per cent. by weight of alcohol. To prepare stronger alcohol, distillation should be repeated several times with quicklime, the final distillation yielding absolute alcohol, which should contain 95 to 99 per cent. of alcohol.

Proof spirit contains 49 per cent. by weight of alcohol. Methylated spirit is rectified spirit to which 10 per cent. of wood spirit, or $\frac{3}{8}$ per cent. of petroleum naphtha, has been added to render it undrinkable; it passes free of duty for manufacturing purposes. Potato spirit made from potatoes, and "corn" spirit made from Indian corn or maize, are common alcohols containing much fusel oil. Still commoner alcohol is made from beet treacle. The three last are made and used largely in Germany.

As has been shown, methylated spirit is a form of alcohol artificially rendered too impure to be used for drinking purposes, and it is passed free of duty for industrial uses. The production of alcohol from malt is a well-known operation; the alcohol is rendered stronger by careful distillation when it passes over and is condensed, while the water and impurities remain in the retort. Even after the most careful distillation the alcohol still contains from 10 to 14 per cent. of water, which can only be removed by very powerful dehydrating agents, such as lime. When freed from this water it is known as absolute alcohol, and has the formula C_2H_6O. Fortu-

nately, however, for most ordinary purposes the ordinary 86 per cent. alcohol is quite strong enough, and this is "denatured" or rendered undrinkable by adding 10 per cent. of wood naphtha, or by adding ½ per cent. to 1½ per cent. of petroleum spirit. Methylated spirit is usually colourless, or pale yellow, with a more or less decided odour due more especially to the naphtha. Its specific gravity is about ·83, and its boiling point about 85° C.

A form of alcohol known as methylated finish is much used by spirit varnish manufacturers; it is prepared by adding 1½ lb. of resin to 1 cwt. of methylated spirit. When mixed with water it resembles milk, and throws down a white precipitate. Methylated finish is much used owing to its cheapness.

Wood spirit is added to spirit varnishes to render them quick-drying. Ether (see below) is also used for the same purpose.

Ether ($C_4H_{10}O$) is formed by the action of strong sulphuric acid upon alcohol. It is a very volatile liquid, boiling at 35° C. It is used in the quick-drying varnishes. Petroleum ether is the very volatile portion which first distils on heating the natural petroleum.

Naphtha, or coal-tar spirit, is in like manner obtained from coal tar by distillation. It is known also as benzene or benzol. Coal-tar naphtha replaces turpentine in common varnish, and is a good solvent for tar and pitch.

Amyl acetate, amyl alcohol, and acetone are also coming into use as solvents for gums in varnish making.

Resin spirit is often used in partial or entire replacement of turpentine in quick-drying or common classes of paint. Resin spirit is the lighter portion of the distillate of resin. Ordinary resin is distilled in an iron retort, and vapour and inflammable gases pass over; these are followed by a light spirit, then heavier resin oils pass over, and a pitch or coke remains in the retort. The resin spirit is usually rectified, the portion having the lowest boiling point being kept as spirit, and the remainder going along with the oils used for preparing resin lubricating greases.

Water is used in a few cases, as, for instance, in the shellac water-varnish, that is, shellac dissolved in borax solution; water is also used as a solvent for gum arabic, sometimes used for glazing purposes.

CHAPTER XV.

VARNISH MANUFACTURE.

The plant used in the commercial manufacture of oil varnishes consists of an oil-boiling pan of iron, either hemispherical or bowl shaped, which is set in brickwork and provided with a fireplace beneath (see Fig. 47, p. 155); this form of boiling pan resembles those that are used for boiling linseed oil (see pp. 25 and 27), and its capacity varies with the amount of varnish made in one operation.

The gum-pot (Fig. 48) is cylindrical, with a flat or rounded bottom; it is constructed of stout copper, the bottom being all in one piece and riveted to the sides. The vessels are usually about 3 ft. deep and 18 in. in diameter, and have a flange about 1 ft. from the bottom. The furnace is usually dug out of the floor of the varnish house, and, for the size of pan mentioned, should be about 28 in. square; its sides are built of best firebricks, on the top of which is placed a level iron plate about 32 in. square and ½ in. thick, having a central hole to admit the bottom of the pan which is supported by the flange. Two handles are also riveted on the sides, about 14 in. from the top of the pan, by means of which it is lifted from the fire. When much varnish is made in one batch, the pans, having a capacity of perhaps 120 gal., are wheeled to and fro, the gum-pot being placed upon an iron carriage provided with wheels (see Fig. 49), so that it can be readily moved about; for further facilitating its motion a line of rails is sunk in the floor of the varnish shed. The furnace is in this case beneath the floor, and circular openings between the rails communicate with it; a gum-melting pot brought over one of these openings is therefore heated by the flames from below.

Furnaces for varnish manufacture vary considerably in construction, each maker having his own methods and his own ideas on the subject. The furnaces for gum running are constructed below the floor of the varnish house, the

top of the furnace being on a level with the floor. The furnaces, built of the best white firebricks, are usually 2 ft. by 3 ft. by 3 ft., and are fired from the outside. A large iron plate 3 ft. 6 in. square and $\frac{3}{4}$ in. thick, with a hole in the centre to admit the bottom of the gum pan, covers the top of the furnace. A copper flange round the bottom of the pan supports it over the hole in the furnace top.

The oil or set copper used for finishing the varnishes holds about 300 gal., and is set in much the same way as an ordinary washing boiler, the only difference being that the finest firebricks are used in construction. Beneath the furnace a trough holding about 30 gal. of water should be constructed ; the wet ashes are used for slaking the fire when the desired temperature is reached.

When the fumes are overpowering, provision should be made for stirring the copper from outside the building, and this can be done by making a hole in the wall above the copper, and covering the hole when not required with an iron slide 30 in. square, which may be pulled up and down as desired. The copper should be provided with a sheet-iron lid worked on hinges and raised by a thin iron chain over a runner above the copper and fastened near the outlet or door so as to be easy of access in case the contents of the copper should ignite.

The stirrer (Fig. 50) is made of copper or iron ; it is shaped at one extremity somewhat like the blade of an oar, and is used for breaking up the gum during the melting down.

Fig. 51 shows a pouring jack, made of copper ; it has a capacity of about two gallons, and is intended to hold the hot oil while the oil is being mixed with the gum. Several other utensils, such as measures, sieves, funnels, etc., are used by the varnish maker, but they do not call for special mention.

The operation of varnish making, like that of oil boiling, is attended with the evolution of a large quantity of noxious fumes, which it is necessary to remove as much as possible from the varnish shed. This is done by providing galvanised iron hoods for the oil-boiling pans and gum-pots, these hoods being connected with galvanised iron tubes which convey the fumes either into the chimney shaft or to the boiler fires ; to facilitate the withdrawal of the

fumes a fan is often used. The hoods are connected to elbow-joints, allowing them to be raised when required; and slides in the front of the hoods allow of access of the stirring-rod, etc. (see Fig. 49).

The operation of varnish making begins with the running of the gum. A quantity of the gum is weighed out, placed in the gum-pot, and heated, being stirred about to prevent charring, until it is in a perfectly fluid condition; at the same time the boiling of the oil is begun, the raw linseed oil being run into the oil-boiling pot and heated to a temperature of about 500° F. for one or two hours. As soon as the gum is quite melted, a measure of the boiling oil is removed from the pan and poured gradually into the gum-pot, while its contents are stirred until all the oil has been added and thoroughly amalgamated with the gum; the contents of the gum-pot are then poured into the set-pot, and another lot of gum is run in the gum-pot. Several runs of gum and oil are in this way placed in the set-pot, the gum rarely being melted in very large bulks, owing to its tendency to darken by the prolonged exposure to heat. When all the gum and oil are in the set-pot, the temperature is raised to the boiling point and the boiling of the varnish is continued until the proper degree of consistency, varying with the nature of the gum and the quality of the varnish required, is obtained.

The quality of the varnish is at this stage observed by placing a few drops upon a piece of glass and noticing if it is quite clear; also by dipping the finger and thumb therein and drawing it out in threads; a good varnish is very extensible, or "strings" well.

The boiling finished, the fire is withdrawn from the set-pot, and when the varnish has cooled somewhat, a certain measure of turpentine is added, so as to thin it down to a workable consistency. When the set-pot is small enough to be removed from the fire, it may be at once carried to an ash heap outside the shed, on which it rapidly cools; in any case, no lights should be near when the turpentine is added, as it gives off an inflammable vapour in large quantities. In fact, at all times the operation of varnish making is a very dangerous one, and special precautions against fire have to be taken. Sand is one of the best materials for putting out a fire arising from boiling oil or

varnish, and it is generally kept on hand in quantity. The above is a general outline of varnish making.

Spirit varnishes are usually made in the cold, or at a very gentle heat, as the gums are readily soluble in the spirit. Methylated spirit is mostly used as the solvent in these varnishes, but in some varnishes, often called volatile oil varnishes, turpentine is employed.

Varnish making on a small scale can only be recommended in the case of naphtha or spirit varnishes. The

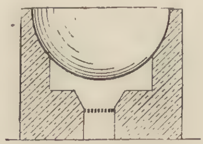


Fig. 47.

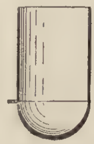


Fig. 48.

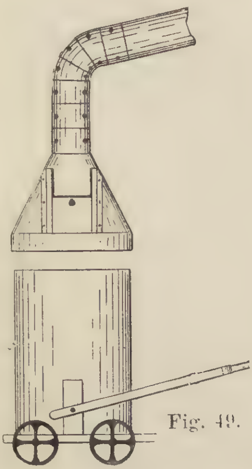


Fig. 49.

Fig. 50.

Fig. 51.

Fig. 47.—Oil-boiling Pan. Fig. 48.—Gum-melting Pan. Fig. 49.—Gum-melting Pot on Wheels. Fig. 50.—Stirring Rod. Fig. 51.—Pouring Jack.

manufacture of oil varnishes, as has been shown, requires special apparatus and knowledge of the properties of the various gums employed.

Spirit varnish simply requires a water bath and the best quality gums. The spirit or naphtha is used merely as a solvent in which the gums and resins are held in solution to enable them to be evenly distributed; when this is done it evaporates, leaving behind a vitreous coating hard or soft, and bright, according to the quantity and quality of gums held in solution. The solid substances are

all of vegetable origin—gums, resins, and gum resins; some dissolve readily, others only partially so; some hard, others soft or bright; hence arises the necessity of mixing them.

For the gums that do not readily dissolve in spirits—such as copal—it is usual to add a quantity of pounded glass; this, it need hardly be said, does not form a part of the varnish itself, but is used as a means of cutting the gums to enable the spirits to penetrate. The gums dissolve more readily by heat; for this purpose a water bath is useful—that is, the vessel containing the gums and spirits should have an outer vessel containing water—glue-pot fashion—so that the materials may be gently brought up to blood heat, not boiled (water-jacketed or steam-jacketed pans answer the purpose best). The gums should be quite dry, crushed up fine, and be frequently stirred up; when dissolved, carefully strain and keep well corked when not in use. Do not let a light get near the spirits when hot, nor keep the cork in tight, for fear of an explosion. It will suffice if a piece of paper or rag is tied over the mouth of the jar till cold.

Shellac dissolved in spirit forms the basis of most spirit varnishes; the addition of resin is often advised on the score of cheapness. It also assists the varnish to flow level, gives it more body, and imparts a brightness not obtainable by the use of shellac alone. As excess of resin yields a varnish easily scratched, benzoin is added for the purpose of increasing its brilliancy. Shellac and spirit alone will suit for some purposes as a varnish.

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